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THE DEGRADATION OF CARBOXYLIC ACIDS INTO ALDEHYDES

REGIOSELECTIVE α-ACETOXYLATION OF 1,2,4-TRIAZOLIUM SALTS WITH DIACETOXYIODATE(I)ANION

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Abstract—A novel method was developed for degradation of carboxylic acid into aldehydes containing one C atom less whose key step consists in α-acetoxylation of 5-alkyl-3-methylthio-1,4-diphenyl-1,2,4-triazolium iodides by (diacetoxyiodo)benzene. The mechanism of the regioselective α-acetoxylation was studied and the diacetoxyiodate(I)anion was shown to be the actual oxidising agent. Further oxidation reactions of tetraethylammonium diacetoxyiodate(I) were investigated.

A novel method was developed for the oxidation of primary alkyl amines into aldehydes by the novel heterocyclic reagent 5-bromo-3-methylthio-1,4-diphenyl-1,2,4-triazolium bromide and diethyl azodicarboxylate.

It has been reported earlier that the addition of the nucleophilic carbene **4** (containing the 1,2,4-triazole skeleton) to aldehydes is reversible. By making use of this reaction, α-hydroxy-carboxylic acids can be degraded with the aid of 1,4-diphenyl-3-methyl-isothiosemicarbazide (**1**) into aldehydes with a chain containing one C atom less.[1-3]

From the point of view of synthesis, the chain-shortening degradation of the carboxylic acids would be more important. This could be realised in principle through 5-substituted 3-(methylthio)-1,4-diphenyl-1,2-4-triazolium salts (**2**),[2] easily obtainable with **1** from carboxylic acids, if these salts could be regioselectively acyloxylated in α-position. In a single case, *viz* that of 3-(methylthio)-1,4-diphenyl-5-propyl-1,2,4-triazolium iodide (**2b**), α-benzoyl-oxylation with dibenzoyl peroxide at −78° was actually successful; however, this reaction could not be generalised.[2]

Several oxidants ($Pb(OAC)_4$, $Tl(OCOCF_3)_3$, *m*-chloroperbenzoic acid, $IO_4^{\ominus}$, $PhSO_2NCl(Na)$ etc) were tested, but only (diacetoxyiodo)benzene proved to be a suitable and generally applicable reagent.[3] (Diacetoxyiodo)benzene has been earlier used for the acetoxylation of active methylene groups.[4]

When iodides **2** or triiodides formed from them with an equimolar quantity of iodine were allowed to react in chloroform with (diacetoxyiodo)benzene, α-acetoxy derivatives (**3**) were regioselectively formed in good yields. Acid catalysed hydrolysis of **3a** gave **5a** and **5b** was similarly obtained from **2b**, without isolation of the intermediate **3b**. Cleavage in the already known way[2,3] of the compounds **5** with methanolic sodium methoxide gives the respective aldehydes. However, for the purposes of degradation the isolation and purification of the intermediates is not necessary: aldehydes can be obtained in one step from the acetoxylation mixture with sodium methoxide.

5-(Acetoxymethyl)-3-(methylthio)-1, 4-diphenyl-1,2,4-triazolium iodide (**8**)[2] was not decomposed by alkali into formaldehyde and **6**. On the other hand, **6** furnished with aqueous formaldehyde solution in the presence of triethylamine the 5-hydroxymethyl derivative (**7**). This observation proves that from **6** is deprotonated even by triethylamine to **4**, the addition of which to formaldehyde is irreversible. The 5-(2-methoxycarbonyl-ethyl) derivative (**2g**) was oxidised with (diacetoxyiodo)benzene into **2h**.

The key step of the degradation is α-acetoxylation. The question arises why only (diacetoxyiodo)benzene is suitable for this purpose, and why oxidation is regioselective. We attempted therefore to elucidate the mechanism of acetoxylation.

First the kinetics of the reaction of **2a**, selected as model compound, with (diacetoxyiodo)benzene was investigated in deuterochloroform solution at 23°. The reaction can be followed by the changes of the ^1H NMR spectrum of the mixture. The reaction was followed up to 71–86% conversion. The selectivity of the reaction is demonstrated by the fact that no signal indicative of any side reaction was found in the ^1H NMR spectrum; neither was a signal characteristic of an intermediate accumulating in detectable quantity observed. The reaction proved to be of first order, the rate of formation of **3a** depending only on the monomolecular decomposition of (diacetoxyiodo)benzene. At 23° the value of the rate constant k_1 is $1.8 \cdot 10^{-4}$ sec^{-1}. From the reaction rates measured at 23, 38 and 48°, the following values were obtained for the activation parameters of the monomolecular decomposition of (diacetoxyiodo)benzene:

$$\Delta H^{\neq}_{38°} = 65.7 \text{ kJ/mol and } \Delta S^{\neq}_{38°} = -95.2 \text{ J/mol K.}$$

The reaction of (diacetoxyiodo)benzene with active

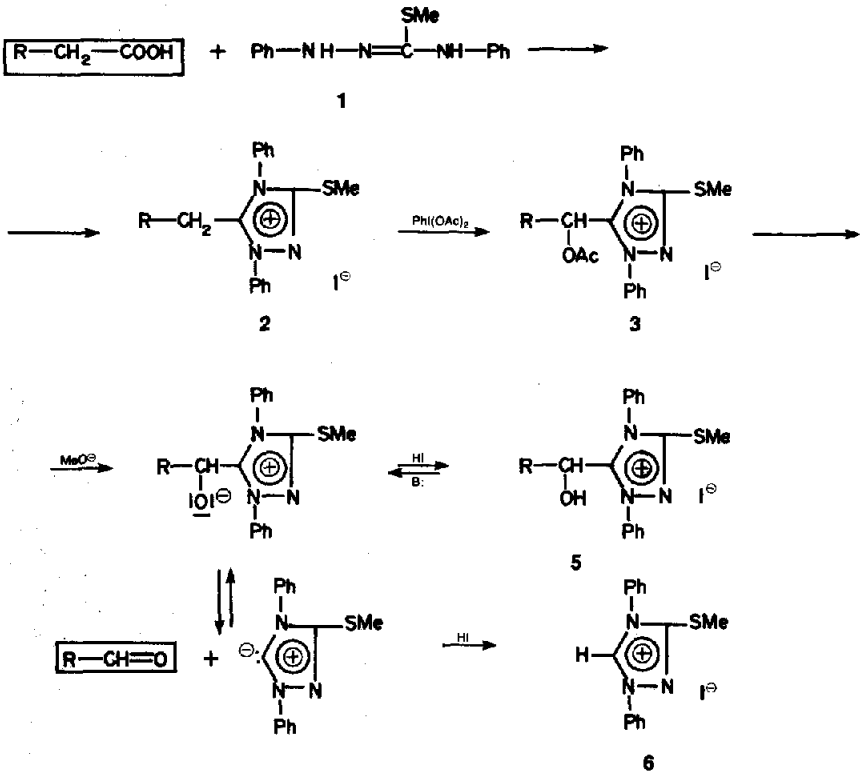

R—CH2—COOH
Ph—NH—N=C(SMe)—NH—Ph
1
Ph(OAc)2
MeO⊖
HI
B:
R—CH=O
2
3
5
6
a: R = Me
b: R = Et
c: R = n-C7H15
d: R = MeOOC—(CH2)3—
e: R = PhCOCH2CH2—
f: R = (Z)—C8H17—CH=CH—(CH2)6—

Fig. 1.

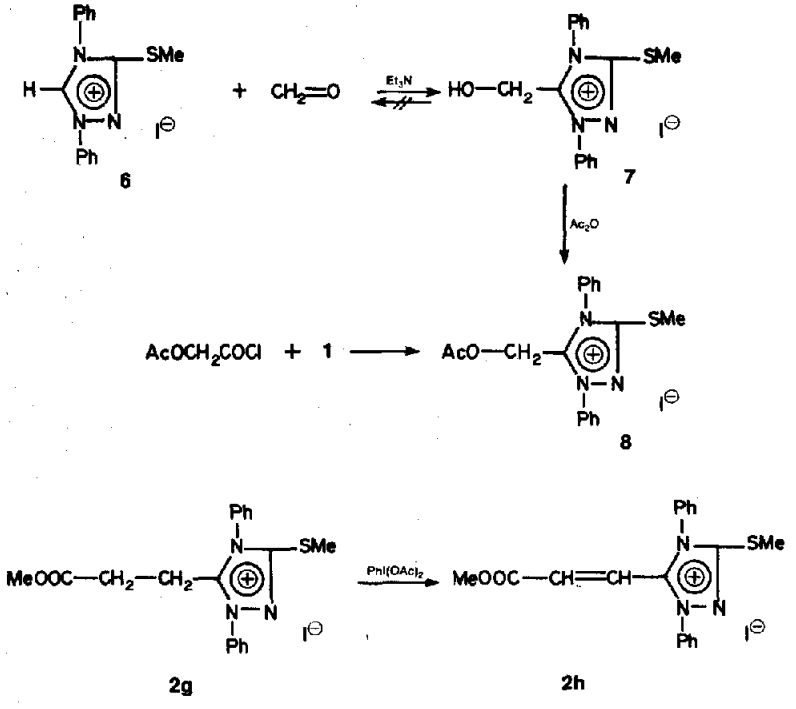

6
CH2=O
Et3N
HO—CH2
7
Ac2O
AcOCH2COCl + 1
AcO—CH2
8
MeOOC—CH2—CH2
MeOOC—CH=CH
2g
2h

Fig. 2.

Me groups has been intepreted[4] by assuming the pre-equilibrium:

$$Ph(OAc)_2 \rightleftarrows Ph\overset{\oplus}{I}OAc + AcO^{\ominus}.$$

Kinetic measurements[5–7] also support this assumption. The equilibrium is strongly shifted towards the covalent form.[5] The alternative monomolecular homolysis of (diacetoxyiodo)benzene:

$$PhI(OAc)_2 \rightleftarrows PhI(OAc)^{\cdot} + AcO^{\cdot} \rightleftarrows PhI + (AcO)_2$$

is ruled out under the conditions used, because, on the one hand, neither (diacetoxyiodo)benzene reacted with 4-iodotoluene, nor 4-(diacetoxyiodo)-toluene[7,8] with iodobenzene and, on the other hand, 10% dibenzoyl peroxide did not catalyse the reaction of **2a** with (diacetoxyiodo)benzene.

On the basis of these findings the kinetic results were interpreted as shown in Fig. 3.

According to literature,[5] the preequilibrium in Fig. 3 is virtually completely shifted towards the direction of the undissociated form. In the presence of **2a**, the concentration of $PH\overset{\oplus}{I}(OAc)$ is of necessity still further decreased, so that the steady state approximation can be used, according to which:

$$\frac{d[3a]}{d\tau} = \frac{k_1 \cdot k_2[PhI(OAc)_2][2a]}{k_{-1}[AcO^{\ominus}] + k_2[2a]}.$$

This is in agreement with the relationship

$$\frac{d[3a]}{d\tau} = k_{measured}[PhI(OAc)_2]$$

found experimentally, if and only if and $k_2[2a] \gg k_{-1}[AcO^{\ominus}]$ and $k_{measured} = k_1$. Taking into consideration the relationship $k_{-1}\,[AcO^{\ominus}] \gg k_1$,[5] it becomes evident that the acetoxylation step (**2a** → **3a**) is a process (or a series of processes) following the rate determining step, so that no conclusions can be drawn from the kinetics of the overall process on the mechanism of the acetoxylation step.

An important observation was that only the **2** triazolium iodides (and the corresponding triiodides) are capable of reacting with (diacetoxyiodo)benzene. Eg. 5-ethyl-3-(methylthio)-1,4-diphenyl-1,2,4-triazolium tetrafluoroborate does not react at all with (diacetoxyiodo)benzene in chloroform solution. This unequivocally indicates that the $Ph\overset{\oplus}{I}(OAc)$ cation formed in the first step rapidly reacts with the *iodide* ion to yield thereby the actual acetoxylation agent. The correctness of this assumption could be easily proved. In chloroform solution, at room temperature, an equimolar mixture of (diacetoxyiodo)benzene and tetraethyl ammonium iodide is converted in excellent yield into iodobenzene and tetraethyl ammonium [diacetoxyiodate(1)](**9**).

$$PhI(OAc)_2 \underset{k_{-1}}{\overset{k_1}{\rightleftarrows}} Ph\overset{\oplus}{I}OAc + AcO^{\ominus}$$

$$I^{\ominus} + Ph\overset{\oplus}{I}OAc \rightleftarrows PhI + IOAc$$

$$Et_4N^{\oplus} + IOAc + AcO^{\ominus} \rightleftarrows Et_4N^{\oplus}I(OAc)_2^{\ominus}$$

9

Fig. 4.

It will be seen in the following that **9** is able to α-acetoxylate triazolium salts of type **2** rapidly.

Compound **9** is an analogue of the Simonini complex $(AgOAc \cdot IOAc)$,[9] which is the reagent used for bringing about the Prévost-oxidation.[10] The Simonini complexes have been known as sources of acetyl hypoiodite. It is important from the point of view of the mechanism of the α-acetoxylation reaction, to determine whether **9** too can be considered only as an acetyl hypoiodite source.

That analytically pure **9** in chloroform solution can be a source of acetyl hypoiodite is proved by the fact that it converts cyclohexene in 82% yield into *trans*-1-acetoxy-2-iodocyclohexane.

$$Et_4N^{\oplus}I(OAc)_2^{\ominus} \underset{k_{-1}}{\overset{k_1}{\rightleftarrows}} Et_4N^{\oplus}AcO^{\ominus} + IOAc$$

9

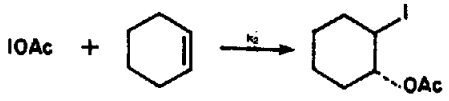


Fig. 5.

This reaction is rather slow and is not catalysed by silver acetate. On the other hand, acetyl hypoiodite,[10] formed in the reaction of silver acetate and iodine, gives with cyclohexene in a rapid exothermic reaction (conversion after 10 min >60%) *trans*-1-acetoxy-2-iodocyclohexane. Thus, the very slow reaction of **9** with cyclohexene means that the equilibrium shown in the last line of Fig. 4 is shifted towards the [diacetoxyiodate(1)] form. In our further work the determination of the value of the rate constant k_1' was thought to be essential. Therefore, the kinetics of the reaction of **9** with cyclohexene in chloroform solution at 23° was studied. The rate of disappearance of **9** was measured by iodometric determination of the amount of **9** in samples taken from

$$PhI(OAc)_2 \underset{k_{-1}}{\overset{k_1}{\rightleftarrows}} Ph\overset{\oplus}{I}OAc + AcO^{\ominus}$$

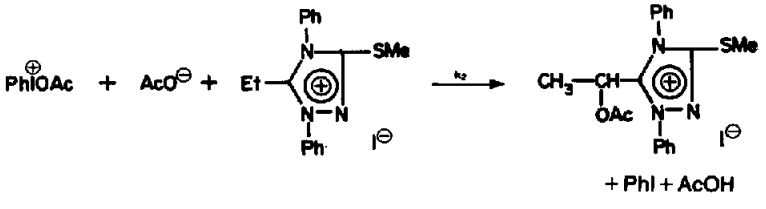


Fig. 3.

the mixture, up to a conversion of 57–60%. The results obtained satisfy a complex equation, which can be linearised in the following form:

$$c_\tau = \ln\frac{a_0}{a} + Q\left(\frac{a_0}{z}\ln\frac{a_0(z+a)}{a(z+a_0)} + \ln\frac{z+a}{z+a_0}\right) \qquad [A]$$

where:

a_0 is the initial concentration of **9**, a is the concentration of **9** at the time τ, a_0+z is the initial concentration of cyclohexene, $a+z$ is the concentration of cyclohexene at the time τ, and c and Q are constants.

This results can be interpreted on the basis of the scheme shown in Fig. 5, in view of the fact the pre-equilibrium in Fig. 5 is strongly shifted towards the [diacetoxyiodate(1)]anion. In the presence of cyclohexene, the concentration of acetyl hypoiodite is of necessity further decreased, thus, the steady state approximation can be used again, from which:

$$-\frac{da}{d\tau} = \frac{k_1' k_2' a(a+z)}{k_{-1}'(a_0-a) + k_2'(a+z)} \qquad [B]$$

where $[AcO^{\ominus}] = a_0 - a$.

The solution of the differential equation B is of form A, if $c = k_1'$ and $Q = k_{-1}'/k_2'$.

The measured value of k_1' was 5.25×10^{-5} sec^{-1} for $Q = 1$. Thus, the tetraethylammonium [diacetoxyiodate(1)] (**9**) induced acetoxylations whose half-life at 23° in chloroform is substantially less than 2.5 hr† can not proceed via acetyl hypoiodite as the reactive intermediate.‡

Returning to the regioselective α-acetoxylation of the triazolium salts **2**, the first problem to be cleared is whether the [diacetoxyiodate(1)anion] is the actual acetoxylating agent.

Since the reaction of 5-ethyl-3-(methylthio)-1, 4-diphenyl-1, 2, 4-triazolium tetrafluoroborate with a 10% excess of **9** at 23° in deuterochloroform solution is so fast that after 5 min only the signals of the α-acetoxy derivative (**3a**) could be observed in the ^{1}H NMR spectrum, it can be taken as proven that the acetoxylating agent is the [diacetoxyiodate(1)]anion itself, rather than the acetyl hypoiodite formed from it.

Thus, we have proved that tetraethyl ammonium [diacetoxyiodate(**1**)] (**9**), the analogue of the Simonini complex is in itself an oxidising, in particular an acetoxylating agent.

Consequently, the mechanism of the regioselective α-acetoxylation of the triazolium iodides **2** may be assumed to be as shown in Fig. 6. The rate determining step is the heterolysis of (diacetoxyiodo)benzene (k_1).

The proposed mechanism is supported by the fact that acetyl hypoiodite formed in the reaction of silver acetate and iodine does not acetoxylate either 5-ethyl-(3-methylthio)-1,4-diphenyl-1,2,4-triazolium tetrafluoroborate, nor the corresponding C-ylide.[2] On the other hand, **9** proved to be an excellent α-acetoxylating agent of the triazolium salts.

The next question concerned, whether monoacetoxylation of the R–CH_2– group takes place in the reaction of the [diacetoxyiodate(**1**)]anion with **2**, and why no α-acetoxy derivative is obtained e.g. from 5-isopropyl-3-(methylthio)-1, 4-diphenyl-1, 2, 4-triazolium iodide[2] or triiodide.

Similar results were obtained when studying the oxidation of other active methylene groups by **9**. Compound **9** rapidly acetoxylates diethyl malonate, as well as ethyl acetoacetate and acetophenone. In the case of diethyl malonate the conversion in chloroform at 23° is higher than 60% within 10 min which shows that also in this case the [diacetoxyiodate(**1**)]anion is the acetoxylating agent. On the other hand, in the case of diethyl n-butylmalonate no change was observed on interrupting the reaction after 10 min but when the mixture was allowed to stand for 12 hr at room temperature, diethyl n-butyliodomalonate was obtained in good yield. Thus, in the latter case acetyl hypoiodite acts as a halogenating agent. This is supported by the value $k_1' = 4.8\times10^{-5}$ sec^{-1} found for the rate constant at 23° in chloroform solution (with $Q' = k_{-1}'/k_2'' = 10$, where k_2'' is the reaction rate constant of the substitution reaction, possibly consisting of several elementary steps).

The presence of two active hydrogens is not absolutely necessary for the acetoxylation reactions of **9**: the planar **6** is also rapidly acetoxylated, the conversion at 23° in chloroform solution being 60% after 10 min. As a result of its enhanced reactivity, resembling that of the active esters (*cf* below), the primary oxidation product **10** is deacetylated under the conditions of work-up, and **11** is formed.

It is probably the bulkiness of the $I(OAc^{\ominus})_2$ anion which inhibits the reaction at trisubstituted tetrahedral C atoms. The H atom which becomes split off and the C atom attached to it are possibly simultaneously attacked by the [diacetoxyiodate(**1**)] anion, so that the reaction proceeds through a 5-membered (or 7-membered) cyclic

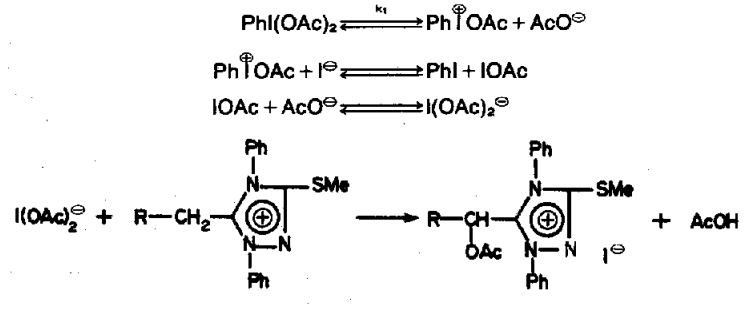
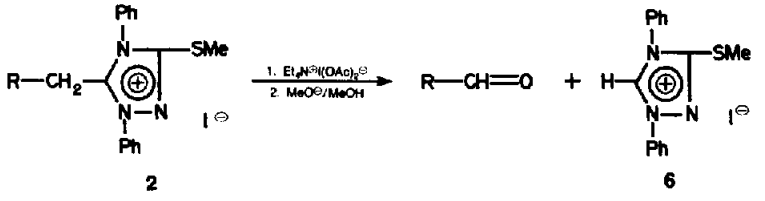


Fig. 6.

†If a larger Q value, e.g. $Q = 3$ is assumed, the straight line obtained from the measured data intersects the abscissa at about 20 min. Even in the case of such gross an error, $k_1' = 7.6\times10^{-5}$ sec^{-1}, i.e. the half-life is 2.5 hr.

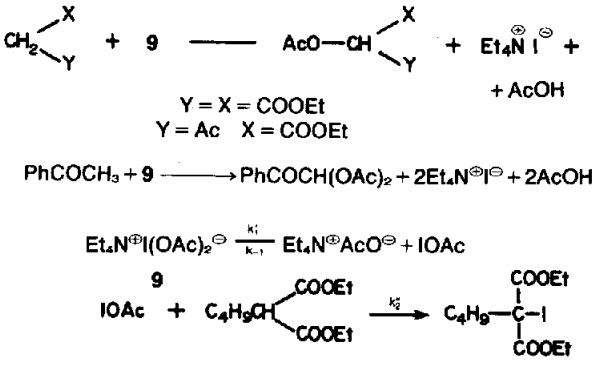
‡Acetic acid does not catalyse the heterolysis of diacetoxy iodate (**1**).



2 6

R = Me
n-C_7H_{15}
(Z)—C_8H_{17}—CH=CH—(CH_2)—

Fig. 7.



Y = X = COOEt
Y = Ac X = COOEt

$PhCOCH_3 + 9 \longrightarrow PhCOCH(OAc)_2 + 2Et_4N^{\oplus}I^{\ominus} + 2AcOH$

Fig. 8.

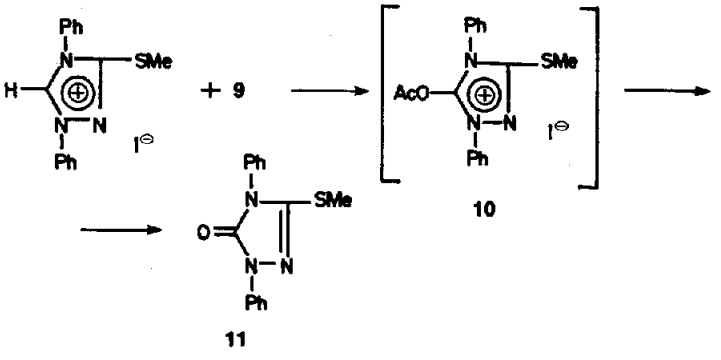


Fig. 9.

transition state. Such a cyclic transition state may be formed only if at least one of the remaining substituents of the tetrahedral C atom is very small, i.e. if at least two H atoms are attached to the latter. The point of interest of this hypothesis is the assumption of a concerted reaction, the course of which the LUMO (σ^*) of the C–H bond interacts with the [diacetoxyiodate(1)] in a way that the HOMO (or HOMOs) of the latter are, similarly to the d orbitals of iridium,[11] simultaneously perturbed by the elements of opposite symmetry of the σ^* orbital. As a result, the substitution should take place with retention since the [diacetoxyiodate(1)] anion attacks the C–H bond in a plane perpendicular to the plane determined by the X, C and the non-reacting H-atoms.

Of course, alternative (e.g. free-radical) mechanism are also possible but, our knowledge concerning the oxidising agent **9** is still insufficient. It is interesting e.g. that contrary to diethyl malonate derivatives, it does not C-acetoxylate ethyl cyanoacetate, and while not reacting with phenolic ethers, it iodinates phenols.

The ability of **9** to oxidise secondary alcohols in homogeneous phase (e.g. chloroform) at room temperature into ketones might be of preparative value. The reaction is slow; for example the rate constant of the oxidation of cyclohexanol into cyclohexanone is $k_1' = 6.4 \times 10^{-5}$ sec^{-1} at 23°. Thus, also in this case the formation of acetyl hypoiodite is the rate determining step. ($Q'' = k_1'/k''' = 4$, where k_2''' is the rate constant of the oxidation step, (itself possibly consisting of several elementary steps). Compound **9** does not oxidise primary alcohols.

In the chain-shortening degradation of carboxylic acids into aldehydes the stability of the nucleophilic carbon split off is also of great importance. The stability of **4** is probably connected with the presence of the 1,2,4-triazolium ring, since e.g. 1,3-dimethyl-2-propylbenzimidazolium iodide (**12**), obtained from N,N'-dimethyl-*o*-phenylenediamine and butyryl chloride, furnishes with sodium hydride and dibenzoyl peroxide a product (**13**), which is only debenzoylated into **14** by sodium methoxide in methanol, while propionic aldehyde is not formed at all.

The triazolium iodides (**2**) can be oxidised in α-posi-

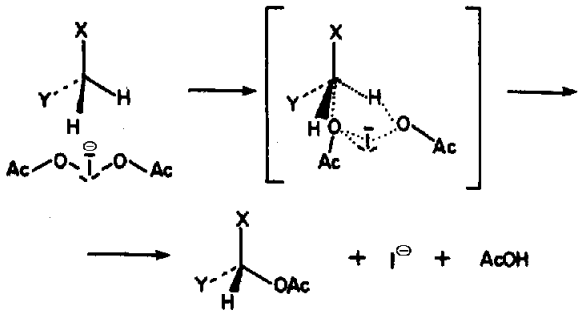


Fig. 10.

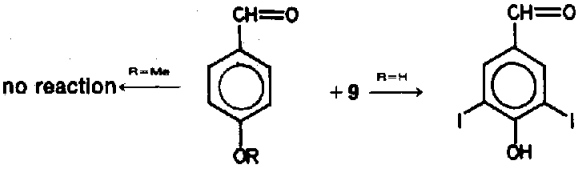


Fig. 11.

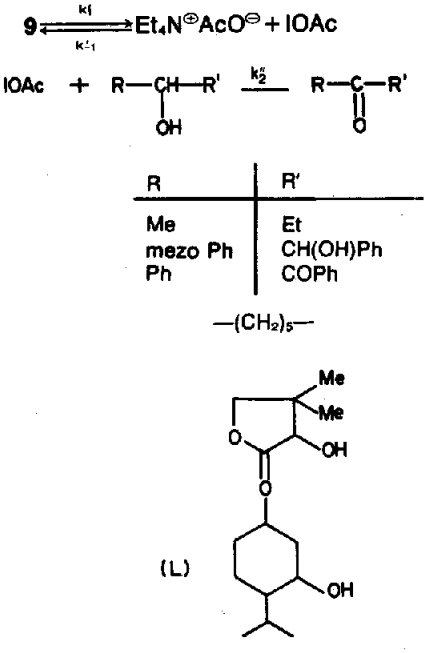


Fig. 12.

tion also with diethyl azodicarboxylate. However, so far all attempts at converting the product **15** into the aldehyde R–CHO failed.

The chain-shortening degradation of carboxylic acids into aldehydes were realised through a more complex route, if the oxidation into aldehydes of the primary amines, obtainable from the acids via the Curtius of Hoffmann degradations, could be performed in good yield. However, up to the present only the oxidation to ketones of primary amines containing *secondary* alkyl groups could be realised in a satisfactory way.[12,13]

The method to be described could be a solution for this problem.[34] in order to carry out their regioselective oxidation, primary amines were masked with the heterocyclic reagent 5-bromo-3-(methylthio)-1, 4-diphenyl-1, 2, 4-triazolium bromide (**16**) and the resulting derivatives **17** were then oxidised in refluxing chloroform with diethyl-azodicarboxylate to obtain the compounds **18**. Treatment of the latter with acid furnished the aldehydes, **19** and diethyl N,N'-hydrazine dicarboxylate.

Compound **16** was obtained from **20**, the latter, in turn, from **1** by successive reaction with formic acid and aqueous potassium bromide. In chloroform solution **20** furnishes with an equivalent amount of bromine the tribromide **21**, which is then converted by triethylamine through the nucleophilic carbene **4** into **16**.

The reactivity of **16** is similar to that of related heterocyclic salts.[14–16] In methanol **16** reacts with sodium methoxide to yield the orthocarbonic acid derivative **23** which was also obtained by sodium methoxide catalysed methanolysis of **22** (obtained from **16** and morpholine). Compound **23** is converted by hot phenylacetic acid into methyl phenylacetate and **11**.

Compound **16** furnishes with benzoic acid in the presence of triethylamine the benzoyloxy derivative **24**, which reacts as a typical active ester. With a second equivalent of triethylammonium benzoate it gives benzoic anhydride, and with aniline it furnishes benzanilide. This explains the formation of **11** on oxidising the iodide **6** with the [diacetoxyiodate(1)]anion (**9**); the intermediate **10** is apparently hydrolysed during work-up.

EXPERIMENTAL

5 - Substituted 3 - methylthio - 1,4 - diphenyl - 1,2,4 - triazolium iodides (**2**)

(a) *3 - Methylthio - 5 - octyl - 1,4 - diphenyl - 1,2,4 - triazolium iodide* (**2c**). Into a mixture of nonanoic acid (20 ml; 114.5 mmol), **1** (29.5 g; 115 mmol) and pyridine (100 ml) phosphoryl chloride (18 ml; 197 mmol) was added dropwise under stirring within about 5 min. Heat was evolved and the mixture started to boil. After cautions decomposition with MeOH (100 ml), aqueous (200 ml) KI (60 g) was added to the hot soln, which was then diluted with water (1800 ml). After cooling, the soln was extracted with dichloromethane (100 ml + 2 × 75 ml), washed with water (120 ml) and evaporated in vacuum. The residue was dissolved in hot EtOAc (120 ml), and allowed to stand overnight in a refri-

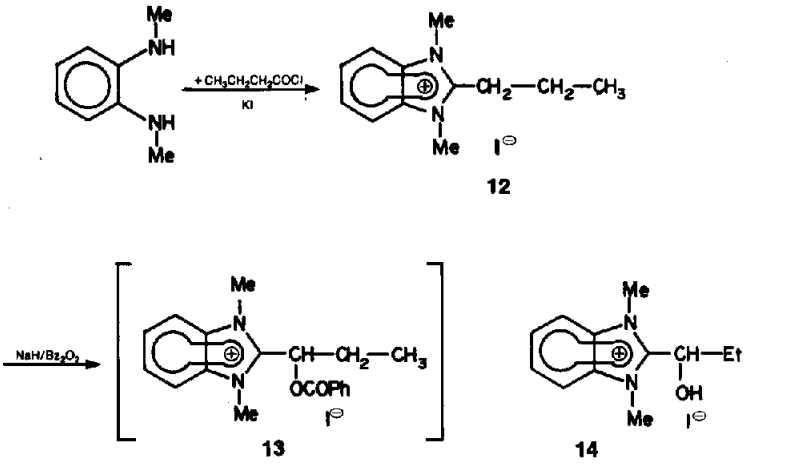


Fig. 13.

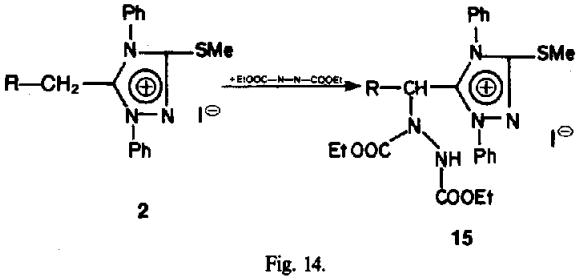


Fig. 14.

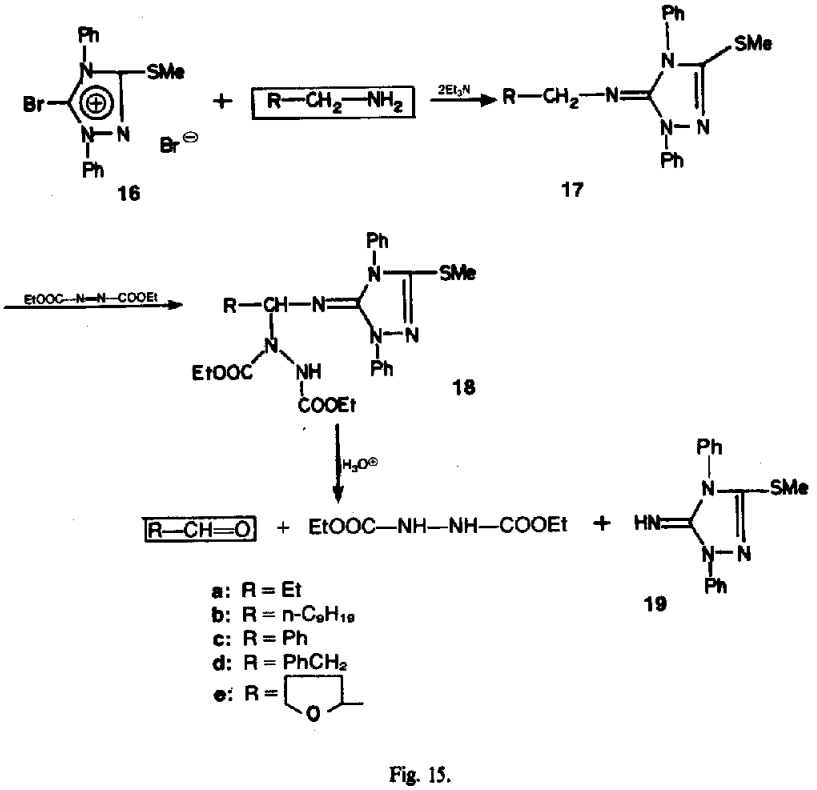


Fig. 15.

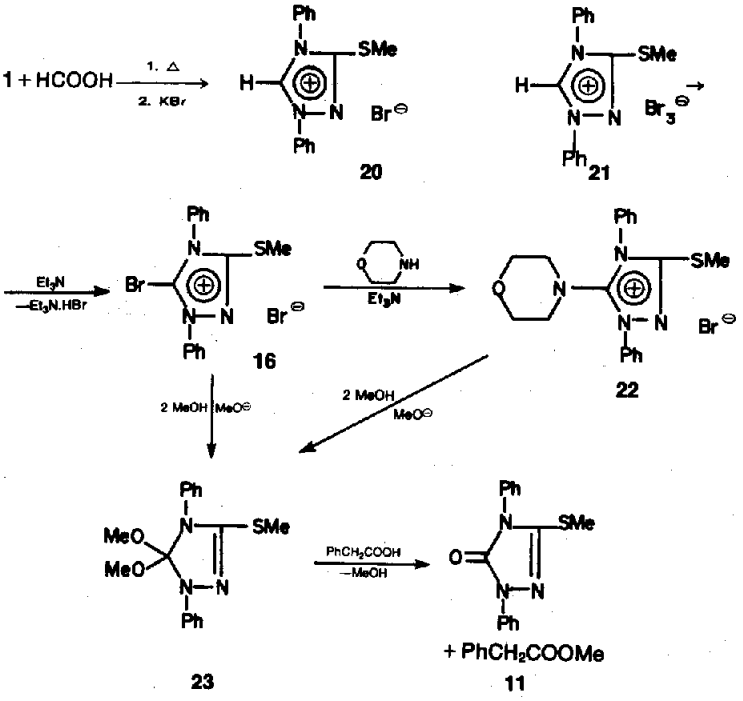


Fig. 16.

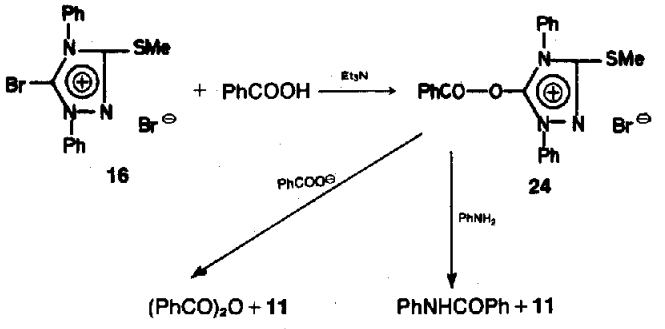


Fig. 17.

gerator. The crystalline product was filtered off, and washed with cold EtOAc (2×20 ml); Yield: 44 g (76%), m.p.: 141–142°. ($C_{23}H_{30}N_3SI$, M.w.: 507.48. Found: N, 8.54. Calc. N, 8.28%); ^1H NMR ($CDCl_3$) δ: 1.0–1.6 m 15H; 2.70 s S–CH_3 3H; 3.15 t 3H; 7.55–7.70 m aromatic-H 6H; 8.1–8.3 m aromatic-o-H 4H.

(b) 5 - (4 - *Methoxycarbonylbutyl*) - 3 - *methylthio* - 1,4 - *diphenil* - 1,2,4 - *triazolium iodide* (2d). Methyl 5-(chlorocarbonyl)pentanoate (27 g; 168.6 mmol), 1 (43.2 g; 168.6 mmol), pyridine (100 ml) and phosphoryl chloride (24 ml; 262 mmol) were allowed to react as described for the preparation of 2c. The mixture was treated with KIaq (480 ml) (120 g) and extracted with dichloromethane (700 ml). The dichloromethane soln was washed with water (2×200 ml) and evaporated. The residue was triturated with ether (2×200 ml), decanted and recrystallised from a mixture of 2-propanol (210 ml) and water (30 ml). (The product was collected after staning for 2 days at 0°), yield: 61.5 g (72%), m.p.: 147°, identical (IR and mixed m.p.) with the product described.[2]

(c) 5 - (3 - *Benzoylpropyl*) - 3 - *methylthio* - 1,4 - *diphenyl* - 1,2,4 - *triazolium iodide* (2e). 3-Benzoylpropionic acid (15 g; 78 mmol),[21] 1 (20 g; 78 mmol), pyridine (50 ml) and $POCl_3$ (11.6 ml = 127 mmol/were allowed to react as described for 2c. The product which separated at 0° from the mixture after treatment with aqueous (100 ml) KI (20 g), was filtered off, washed with water (2×50 ml), 2-propanol (2×20 ml) and ether (2×50 ml), and dried in air at 80°, yield: 37 g (88%), m.p.: 229–230° (from abs MeOH). ($C_{25}H_{24}N_3SOI$, M.w.: 541.45. Found: N, 7.61. Calc. N, 7.76%). ^1H NMR ($CDCl_3$) δ: 1.9 m, β-CH_2; 2.65 s, S–CH_3 3H; 2.85 t, γ-CH_2 2H; 3.30 t, α-CH_2 2H; 7.3–7.8 m aromatic H 11H; 8.0–8.3 m aromatic-o-H 4H.

(d) 5 - [(Z) - *Heptadec* - 8 - *en* - 1 - *yl*] - 3 - *methylthio* - 1,4 - *diphenyl* - 1,2,4 - *triazolium iodide* (2f). Oleic acid (110 g; 389 mmol), 1, (100 g; 388.6 mmol), pyridine (300 ml) and $POCl_3$ (55 ml; 600 mmol) were allowed to react as described for 2c. The mixture was then treated with KIaq (600 ml; 200 g), diluted with water (1000 ml), and allowed to stand overnight at 0°. The crystalline product was filtered off, washed with water (2×200 ml), and dissolved in dichloromethane (600 ml). The dichloromethane soln was dried, and evaporated to dryness. The residue was dissolved in EtOAc (200 ml). The soln was allowed to stand overnight at 0°. The product was filtered off and washed with ice-cold EtOAc (2×50 ml), yield: 196 g (80%), m.p.: 114°. ($C_{32}H_{46}N_3SI$, M.w.: 631.7. Found: N, 6.71; Calc. N, 6.65%). ^1H NMR ($CDCl_3$) δ: 1.0–1.3 m, 25H; 1.8–2.1 m, 4H; 2.70 s, S–CH_3 3H; 3.15 t, α-CH_2 2H; 5.3 m, CH=CH 2H; 7.55–7.7 m aromatic-H 6H; 8.1–8.3 m aromatic-o-H 4H.

5 - (1 - *Acetoxyethyl*) - 3 - *methylthio* - 1,4 - *diphenyl* - 1,2,4 - *triazolium iodide* (**3a**)

(a) *A mixture of* **2a** (*5 g; 11.8 mmol*),[2] (diacetoxyiodo)*benzene* (3.86 g; 12 mmol)[17,18] and chloroform (30 ml) was allowed to stand overnight at room temp, diluted with dichloromethane (50 ml), shaken with an aqueous (100 ml) soln of sodium hydrosulfite (5 g), AcOH (5 ml) and KI (20 g), washed with water (2 × 50 ml) and evaporated in vacuum. The residue was triturated with ether (2 × 30 ml), decanted and recrystallised from a mixture of EtOH (10 ml) and EtOAc (20 ml). The recrystallised product was collected after being allowed to overnight in a refrigerator, yield: 3.4 g (60%), m.p.: 187–188°. ($C_{19}H_{20}N_3SiO_2$, M.w.: 481.36. (Found: C, 47.60; H, 4.35; I, 26.13. Calc. C, 47.41; H, 4.19; I, 26.37%); IR: νC=O: 1760 cm^{-1}; ^1H NMR ($CDCl_3$) δ: 1.75 d, CH_3 3H; ,95 s, CH_3CO 3H; 2.75 s, CH_3S 3H; 4.75 q, –CH–O 1H; 7.55–7.75 m aromatic-H 6H; 8.05–8.25 m aromatic o-H 4H.

(b) To a refluxing mixture of **2a** (42.3 g = 100 mmol), I_2 (28 g = 110 mmol) and chloroform (250 ml)† a mixture of (diacetoxy iodo)benzene 38.6 g = 120 mmol) and chloroform (250 ml) was added dropwise within 15 min. Refluxing was continued for further 30 min. After cooling, the mixture was thoroughly shaken with an aqueous (300 ml) soln of sodium hydrosulfite (45 g), KI (90 g) and AcOH (30 ml), washed with water and evaporated in vacuum. Dichloromethane (200 ml) was added and distilled off, in order to remove traces of water. The residue was triturated with ether (250 ml), cooled to 0°, filtered off, and washed with ether (2 × 100 ml). The crude product was dissolved in a hot mixture of EtOAc (80 ml) and EtOH (40 ml), hot EtOAc (80 ml) was added, and the mixture was allowed stand overnight at 0°. The yellow crystals were filtered off, washed with EtOAc and ether, and dried in air, yield: 29.4 g (61%). The product proved identical (IR, m.p., mixed m.p.) with that obtained according to (a).

(c) A mixture of 1 (20 g; 78 mmol),[2] propionic acid (5.7 ml; 78 mmol) and pyridine (40 ml) was allowed to react with $POCl_3$ (11 ml; 120 ml) as described for the preparation of **2c**. Hot aqueous (200 ml) sodium tetrafluoroborate (30 g) was added, and the product which separated on cooling was filtered off, and recrystallized from EtOH, yield: 18 g (60%), m.p.: 188–189°. (The product gives with 20% KIaq in dimethyl formamide **2a**.) The ^1H NMR spectrum of the resulting 5-ethyl-3-(methylthio)-1, 4-diphenyl-1, 2, 4-triazonium tetrafluoroborate was identical with that of **2a**: ($CDCl_3$) δ: 0.96 t, CH_3 3H; 2.70 s, CH_3S 3H; 3.20 q, CH_2 2H; 7.6–7.8 m aromatic-H 6H; 8.25–8.45 m aromatic-o-H 4H.

A mixture of 5 - ethyl - 3 - (methylthio) - 1,4 - diphenyl - 1,2,4 - *triazolium tetrafluoroborate* (*3.65 g; 9.5 mmol*), and *chloroform* (25 ml) was stirred at room temp for 10 min with tetraethylammonium [diacetoxyiodate(1)] (**9**) (3.75 g; 9.5 mmol); the mixture was diluted with chloroform, thoroughly shaken with an aqueous (100 ml) soln of $NaHSO_3$ (5 g) and KI (20 g), washed with water (2 × 50 ml), and dried over $CaCl_2$. Evaporation to dryness in vacuum furnished an oil which when triturated with ether (50 ml) transformed into a powder. This was filtered off, dissolved in a hot mixture of EtOH (7 ml) and EtOAc (15 ml) was added and the soln was allowed to stand overnight at 0°.

The resulting crystalline product was filtered off and washed with cold EtOAc and ether, yield: 3.2 g (70%). The product proved identical (m.p., mixed m.p., IR) with that obtained according to (a).

Neither 5 - ethyl - 3 - (methylthio) - 1,4 - diphenyl - 1,2,4 - triazolium tetrafluoroborate, nor the C-ylide[2] obtained from it with sodium hydride, reacted with (diacetoxyiodo)benzene in the way described either in section (a) or in section (b) to furnish the α-acetoxy derivative.

5 - (1 - *Hydroxyethyl*) - (*methylthio*) - 1,4 - *diphenyl* - 1,2,4 - *triazolium iodide* **5a**)

The crude **3a**, obtained from a mixture of **2a** (3.5 g; 8.26 mmol), (diacetoxyiodo)benzene (2.9 g; 9 mmol) and chloroform (30 ml) as described above in section (a) was refluxed with a mixture of MeOH (20 ml), conc HCl (10 ml) and water (10 ml) for 2 hr. The mixture was evaporated to dryness in vacuum. The residue was dissolved in a hot mixture of MeOH (30 ml) and water (10 ml), and hot aqueous (40 ml) KI (10 g) was added. The soln was cooled to 0°; the product which separated was filtered off, and washed with water, 2-propanol and ether, yield: 3.1 g (85%), m.p.: 192–193°. The product proved identical (m.p., mixed m.p., IR) with the compound described.[2]

5 - (1 - *Hydroxypropyl*) - 3 - *methylthio* - 1,4 - *diphenyl* - 1,2,4 - *triazolium iodide* (**5b**)

A *mixture of* **2b** (*10 g; 22.9 mmol*),[2] I_2 (6.1 g; *24 mmol*) and chloroform (40 ml) was allowed to react with (diacetoxyiodo)benzene as described for the preparation of **3a** (section (b)). The residue obtained after evaporation of the solvent was triturated with ether (2 × 100 ml), decanted, refluxed 1 hr with a mixture of MeOH (40 ml), water (20 ml) and conc HCl (20 ml). The mixture was again evaporated to dryness in vacuum. The residue was dissolved in a hot mixture of MeOH (100 ml) and water (10 ml), aqueous (150 ml) KI (30 g) was added and the soln was cooled to 0°. The resulting product was filtered off and washed with water, yield: 7.2 g (69%), m.p.: 212–213° (from EtOH containing AcOH). ($C_{18}H_{20}N_3OSI$, m.p. 453.35; Found: N, 9.73; I, 28.34. Calc. N, 9.27; I, 28.00%). ^1H NMR ($CDCl_3$) δ: 0.80 t CH_3 3H; 1.5–2.0 m CH_2 2H; 2.75 s, S–CH_3 3H; 4.7–5.2 m, OH and CH 2H; 7.5–7.7 aromatic H 6H; 8.05–8.2 aromatic-o-H 4H.

Preparation of aldehydes from **2c–2f** *triazolium salts—octanal*

(a) The crude product obtained from a mixture of **2c** (65 g; 128 mmol), I_2 (34.5 g; 135 mmol) and chloroform (100 ml), as described for the preparation of **3a** according to (b) was repeatedly evaporated with CH_2Cl_2 (300 ml), stirred for 2 min with hot ether (300 ml) and cooled to 0°. The solvent was decanted, the residue with ether stirred (2 × 100 ml). (On washing the combined either solns with water, drying over $CaCl_2$ and evaporating the ether, 90% of iodobenzene was obtained.) The residue was dissolved in dry hot MeOH (75 ml). NaOMe (5.4 g; 100 mmol) in dry MeOH (100 ml) was added, and the mixture was allowed to stand for 15 min at room temp. The soln was then acidified with a mixture of KI (40 g) conc H_2SO_4 (15 ml) and water (200 ml), and subjected to steam distillation. The distillate (about 600 ml) was extracted with ether (400 ml), washed with water (3 × 100 ml), and dried over $CaCl_2$. The ether was evaporated. The residue (10.1 g = 61%) was distilled off, b.p.: 168–170°, yield: 8.2 g (50%). The product was identified in the form of its 2,4-dinitrophenylhydrazone,[19] m.p.: 105°.

The residue of the steam distillation was cooled to 0°, the substance which separated was filtered off and recrystallized from EtOH, yield: 1.6 g **6** (31%), m.p.: 248–250°, identical (IR, m.p., mixed m.p.) with the product described.[2]

(b) A mixture of **2c** (40 g; 78.8 mmol), **9** (40 g; 106 mmol) and chloroform (100 ml) was allowed to stand overnight, the substance which separated was filtered off, and washed with chloroform (2 × 20 ml) to obtain 13 g (63%) of tetraethylammonium iodide. The chloroform filtrate was diluted with chloroform (200 ml) and worked up according to section (a), yield: 4.2 g (41%) of octanal and 12 g (38%) of **6**.

The distillate, obtained from **3a** by treatment with NaOMe-MeOH as described in section (a) and subsequent steam distillation, gave a 2,4-dinitrophenylhydrazone of *propanal*, yield: 59%, m.p.: 155°.[19] In this case, **6** can be obtained in 55% yield.

Methyl 4-formylbutanoate

A mixture of **2d** (48 g; 94.3 mmol), I_2 (25.4 g; 100 mmol) and chloroform (100 ml) was allowed react with a mixture of (diacetoxyiodo)benzene (35.4 g; 110 mmol) and chloroform (350 mmol) and the mixture was worked up as described for the preparation of octanal. The crude product was dissolved in dry MeOH (100 ml), allowed to stand for 15 min with a mixture of NaOMe (4 g; 75 mmol) and dry MeOH (50 ml); subsequently a mixture of AcOH (15 ml) and ether (200 ml) was added. The mixture was cooled to 0°, shaken with aqueous (700 ml) KI (50 g). The ether phase was separated and the aqueous phase was extracted with ether (2 × 150 ml). The combined ethereal solns were washed with water (2 × 75 ml), 5% $NaHCO_3$aq (2 × 50 ml) and water (2 × 50 ml), dried over $CaCl_2$. The ether was

†On adding ether (300 ml) to this soln, the corresponding triiodide separates, m.p.: 137°.

evaporated and, the resulting dark brown oil was distilled in vacuum, b.p.: 106–108°/25 mm Hg, yield: 6.3 g (51%). The 2,4-dinitrophenylhydrazone (m.p. 105–106) proved identical (mixed m.p., IR) with the product described.[20]

From the aqueous-methanolic mother liquor **6** can be isolated, yield: 13 g (35%).

(Z)-Hexadec-8-enal

(a) To the refluxing mixture of **2f** (175 g; 277 mmol), I_2 (73.6 g; 290 mmol) and chloroform (300 ml) the soln of (diacetoxyiodo)benzene (96.6 g; 300 mmol) in chloroform (700 ml) was added dropwise with stirring within 15 min; refluxing was continued for 30 min. The mixture was thoroughly shaken with a mixture of $NaHSO_3$ (150 g), KI (300 g), AcOH (75 ml) and water (800 ml), washed with water (2 × 500 ml), and evaporated to dryness in vacuum. The residue was taken up in CH_2Cl_2 (400 ml) the soln was evaporated to dryness, the residue stirred with hot hexane (300 ml) for 5 min and cooled to 0°. The soln was decanted, the residue was taken up in dry ether (300 ml) and the soln allowed to stand overnight at 0°. The ether was decanted from the brown oil which had separated; the oil was dissolved in dry MeOH (150 ml), NaOMe (10 g; 200 mmol) and dry MeOH (100 ml) were added and the mixture was allowed to stand for 45 min. The soln was then shaken with a mixture of water (1000 ml), conc H_2SO_4 (25 ml) and pentane (600 ml). After filtration the pentane soln was separated, the aqueous phase was extracted with pentane (2 × 300 ml), the combined pentane solns were washed with water (2 × 200 ml), 10% HCl (2 × 200 ml), water (2 × 200 ml), 5% $NaHCO_3$aq (2 × 200 ml), and water (2 × 200 ml), and dried over $CaCl_2$. The solvent was distilled off and the residue (40.6 g) was fractionated in vacuum, b.p.: 37–38°/3 mm Hg) iodobenzene (IR), and b.p.: 138–142 (3 mm Hg), 16.8 g (24%) (Z)-hexadec-8-enal.

Identification

A mixture of (*Z*)-hexadec-8-enal (8 g; 31.7 mmol), 6-(2-aminophenyl)-3-methylthio-1, 2, 4-triazin-5(2H)-on (5.8 g; 25 mmol)[22] and EtOAc (50 ml) was heated to its b.p., and the red resulting soln allowed to stand for 3 hr at room temp. After cooling to 0°, the orange yellow crystalline needles separated were filtered off, and washed with EtOAc (10 ml) and pentane (2 × 20 ml), yield: 7.1 g (80%), m.p.: 103°, 6-[(Z)-hexadec-8-en-1-yl] - 6.7 - dihydro-3-methylthio-[1,2,4]triazino[1,6-c]quinazolin-5-ium-olate.
($C_{27}H_{40}OS$, M.w.: 468.69. Found: N, 12.19; S, 7.03. Calc. N, 11.96; S, 6.84%). ^{1}H NMR ($CDCl_3$) δ: 0.9 m, 3H 1.3 s, 22H; 2.0 m, 4H; 2.55 s, SCH_3 3H; 5.3 m, CH=CH 2H; 5.7 m, NH 1H; 6.9–7.4 m aromatic-H and –CH– 4H; 9.0 m aromatic-H 1H.

(b) A mixture of **2f** (164 g; 260 mmol), **9** (100 g; 292 mmol) and chloroform (200 ml) was stirred at room temp for 1 hr, and allowed to stand for 24 hr. The tetraetethylammonium iodide which separated (52 g; 78%) was filtered off and washed with chloroform (2 × 40 ml). The filtrate was diluted with chloroform (400 ml) and thoroughly shaken with a soln of $NaHSO_3$ (50 g), KI (60 g), AcOH (60 ml) and water (600 ml), washed with water (2 × 400 ml), and evaporated in vacuum. CH_2Cl_2 added to the residue and distilled off in order to remove traces of water present. The hot residue was taken up in 300 ml hot hexane, and the mixture cooled to 0°. The solvent was decanted, and the residue was triturated with ether (500 ml), and allowed to stand for 1 hr at 0°. The ether was then decanted from the brown oil. The oil substance was dissolved in dry MeOH (160 ml), a soln of NaOMe (9.2 g; 170 mmol) in dry MeOH (80 ml) was added and the mixture allowed to stand for 30 min at room temp. From here on, the procedure was identical with that described in section (a). The residue obtained after distillihg off the n-pentane (33.6 g, 51%) was distilled in vacuum, b.p.: 118–120° (2 mm Hg), yield 20.4 g (31%).

By adding KI (100 g) and water (500 ml) to the aqueous-methanolic-sulfuric acid mother liquor, 38 g (37%) of **6** were obtained.

5 - (Hydroxymethyl) - 3 - methylthio - 1,4 - diphenyl - 1,2,4 - triazolium iodide (7)

The mixture of an aqueous (60 ml) soln of **6** (29 g; 73.4 mmol) triethylamine (5 ml; 36 mmol) and 37% formaldehyde (60 ml) was stirred under water-cooling for 1 hr, and acidified with AcOH (10 ml). The insoluble product was filtered off, washed with water (2 × 20 ml) and EtOH (2 × 20 ml) and dried on air at 80°, yield: 24.5 g (78%), m.p.: 204–205°C (from MeOH). ($C_{16}H_{16}N_3SOI$, M.w.: 425.3. Found: I, 29.98. Calc. I, 29.84%). ^{1}H NMR (TFA) δ: 2.35 s SCH_3 3H; 4.65 s, CH_2 2H; 7.2 s aromatic –H 10H.

5 - (Acetoxymethyl) - 3 - methylthio - 1,4 - diphenyl - 1,2,4 - triazolium iodide (8)

Compound **7** (2 g; 4.7 mmol) was dissolved in Ac_2O (10 ml; 106 mmol) by refluxing for a few min. After cooling, the crystalline product was filtered off, and washed with 2-propanol and ether, yield: 1.1 g (50%), m.p.: 182–183°. The product proved identical (mixed m.p., IR) with that described.[2]

5 - [2 - (E) - Methoxycarbonylvinyl) - 3 - (methylthio)] - 1,4 - diphenyl - 1,2 - 4 - triazolium iodide (**8**)

A mixture of **2g** (5 g; 10.38 mmol),[2] (diacetoxyiodo)benzene (3.98 g; 12 mmol) and chloroform (50 ml) was allowed to stand for a day, then shaken thoroughly with a mixture of $NaHSO_3$ (5 g), KI (20 g), AcOH (5 ml) and water (100 ml), washed with water (2 × 50 ml), and evaporated in vacuum. The residue was dissolved in CH_2Cl_2 (50 ml), and the soln again evaporated. The residue triturated with ether (50 ml), filtered, and washed with ether, yield: 4.8 g (96%), m.p.: 223–224°, dec. (from MeOH). ^{1}H NMR ($CDCl_3$) δ: 2.6 s, SCH_3 3H; 3.55 s, OCH_3 3H; 6.05 and 7.15 m, CH=CH 2H; J = 17 Hz; 7.50–7.65 m aromatic H 6H; 8.0–8.30 m aromatic o-H 4H.

Kinetic measurements

Reaction of **2a** *with (diacetoxyiodo)benzene.* Precisely weighed anal. pure **2a**[2] and (diacetoxyiodo)benzene[17,18] were dissolved in 0.5 ml $CDCl_3$, and the changes of the ^{1}H NMR spectrum was followed with a JEOL Model PS-100 instrument in a cell thermostated within ±0.5°.

The quantity of **3a** formed was determined by measuring the integral of the δ = 0.96 triplet (the Me triplet of the Et group of **2a**) and the integral of the appearing δ = 1.75 doublet (doublet of the Me group of the –CH(OAc)Me group of **3a**) in the ^{1}H NMR spectrum. Bands characteristic of the formation of other products could not be detected during the reaction, so that the sum of the two integral values was taken as 100%; the value of the integral of the doublet was referred to this value, and from the known initial concentrations, the concentrations of **3a** and (diacetoxyiodo)benzene were calculated on this basis.

As an example, the ^{1}H NMR spectra recorded at 23° at reaction times 6, 20 and 40 min, and the tabulated concentration values obtained for **3a** are presented for the initial concentrations [**2a**] = 0.2 mol/1 and [PhI(OAc)$_2$] = 0.2 mol/1.

The results obtained were linearized on the basis of the following equation:

$$\ln \frac{[PhI(OAc)_2]_0}{[PhI(OAc)_2]-[3a]} = k_1\tau.$$

Values of the rate constant k_1 measured at different initial concentrations are shown in the following table (t = 23°).

Measurements carried out at 38° and 48° gave values of $k_{-1} = 6.25 \times 10^{-4}$ sec^{-1}, and $k_{-1} = 1.6 \times 10^{-3}$ sec^{-1}, respectively. From the rate constants measured at 23, 38 and 48° $\Delta H^{\neq}_{38°} = 65.7$ kI/mol was of the Arrhenius equation obtained by malling use. The equation $\Delta S_T^{\neq} = 4.574 \times [1\,g\,k + \Delta H^{\neq}/4.574T - 1\,g\sqrt{2.08 \cdot 10^{10}T}]$, then leads to a value of −95.2 I/mol K $\Delta S^{\neq}_{38°}$.

In the presence of an equimolecular amount of iodine a value of $k_1 = 4.25 \times 10^{-4}$ sec^{-1} was obtained at 23°.

In the presence of 10% benzoyl peroxide, $k_1 = 2.4 \times 10^{-4}$ sec^{-1} was obtained.

Reaction of tetraethyl ammonium diacetoxy iodate(1) (**9**) *with cyclohexene.* Analytically pure cyclohexene and **9** were used. The initial cyclohexene concentration was determined by precise weighing, the concentration of **9** by iodometric titration of the soln.

2 ml of the soln of **9** (c_0 = 0.4–0.7 mol(1)) in 50 ml chloroform was thoroughly shaken with 30 ml of 0.1 N $Na_2S_2O_3$ soln, until

Table 1.

min.	3a mol/l	min.	3a mol/l	perc	3a mol/l
9	0,0256	24	0.0520	50	0.1000
10	0,0264	27	0,0560	55	0,1044
11	0,0272	30	0,0647	60	0,1101
14	0,0394	36	0,0735	68	0,1213
18	0,0428	40	0,0812	75	0,1303
20	0,0496	45	0,0912		∅

Table 2.

2a Co = mol/l \ PhI(OAc)$_2$ C_o=mol/l	0,1	0,15	0,2	0,3	0,4
0,1	$1,51.10^{-4}$ sec^{-1}	$1.35.10^{-4}$ sec^{-1}	$2.25.10^{-4}$ sec^{-1}	$1,52.10^{-4}$ sec^{-1}	$2.15.10^{-4}$ sec^{-1}
0,2			$2.13.10^{-4}$ sec^{-1}		$1.85.10^{-4}$ sec^{-1}
0,4					$2.06.10^{-4}$ sec^{-1}

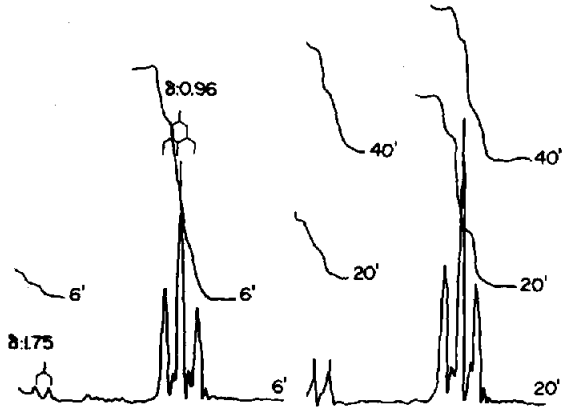


Fig. 18.

the two-phase mixture became colourless (15–30 sec) whereby the [diacetoxaiodate(1)] was reduced to iodide:

$$2Na_2S_2O_3 + Et_4N^{\oplus}_{9}I(OAc)_2^{\ominus} \rightarrow Na_2S_2O_6 + 2NaOAc + Et_4N^{\oplus}I^{\ominus}.$$

The mixture was then acidified with 4 ml of 10% HCl, and immediately titrated with 0.1 m $KH(IO_3)_2$ soln.

The concentration of **9** was calculated with the aid of the following equation:

$$[9]\ mol/l = 25[30 - 0.1\ n\ KH(10_3)_2\ soln\ consumed\ (ml)] \times 10^{-3}\ mol/l.$$

The results were checked with the aid of a calibration diagram plotted for precisely weighed quantities of **9**, cyclohexene and *trans*-1-acetoxy-2-iodocyclohexane.

The measurements were carried out in an ultrathermostat at 23 ± 0.5° in chloroform soln. From the mixture (50 ml) samples of 2 ml were taken, and the **9** content of the samples was determined by iodometric titration as described.

As an example, the results of the measurements are given, in which the initial concentration of **9** was 0.512 mol/l, and that of cyclohexene 0.730 mol/l.

The results were linearized on the basis of the following equation:

$$k_1' = \ln\frac{a_0}{a} + Q\left(\frac{a_0}{z}\ln\frac{a_0}{a}\frac{(z+a)}{(z+a_0)} + \ln\frac{z+a}{z+a_0}\right)$$

where a_0 is the initial concentration of **9**, $z+a_0$ is the initial concentration of cyclohexene and $Q = (k_1'/k_2')$ is a dimensionless number.

The results are shown in Fig. 20.

The k_1' values measured at various initial concentrations for $Q = 1$ are listed in Table 4.

In the presence of an equimolar amount of AcOH at 23° in chloroform soln a value of $k_1' = 6.2 \times 10^{-5}\ sec^{-1}$ was obtained ($Q = 0$).

The rate of the reaction of **9** with diethyl butylmalonate was determined in a similar way. In this case a value of $k_1' = 4.8 \times 10^{-5}\ sec^{-1}$ was found for the rate constant for $Q = k_1'/k_2'' = 10$ at 23°.

The rate of the reaction **9** with cyclohexanol was determined in a similar way. In this case the value of the rate constant was $k_1' = 6.4 \times 10^{-5}\ sec^{-1}$ for $Q = k_1'/k_2'' = 4$ at 23°C. Here (because of an oxidative side-reaction, *viz* formation of tetraethyl ammonium triiodide and which gradually separated from the mixture and made further measurements impossible) the reaction could be followed only up to a conversion of 40%.

9 ($c_0 = 0.37$ mol/l) and diethyl malonate ($c_0 = 0.4$ mol/l) reacted so rapidly in chloroform that after 10 min 60% of **9** were already used up. Similar results were obtained for the reaction of **9** ($c_0 = 0.58$ mol/l) with **6** ($c_0 = 0.506$ mol/l) in chloroform at 23°. After 10 min 60% al were already used up.

Tetraethylammonium [*diacetoxyiodate*(1)] (**9**). A mixture of tetraethylammonium iodide (20 g; 78 mmol), (diacetoxyiodo)benzene (25 g; 80 mmol) and dry chloroform (100 ml) was

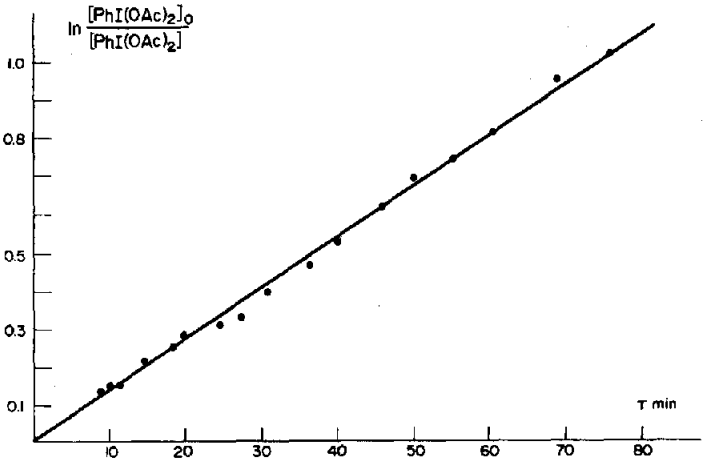


Fig. 19.

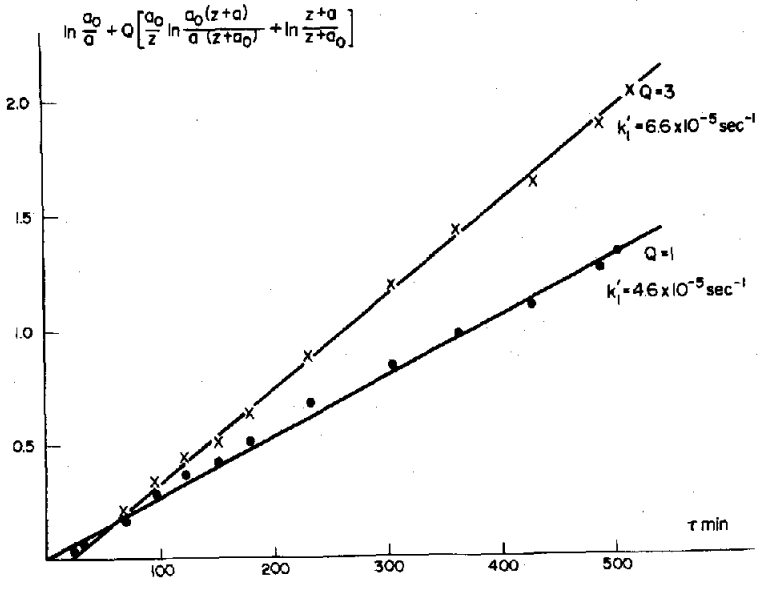


Fig. 20.

Table 3.

min	$C_{Et_4\overset{+}{N}\ I(OAc)_2^-}$	min	$C_{Et_4\overset{+}{N}\ I(OAc)_2^-}$
20	0,4970	180	0,3275
30	0,4825	240	0,2875
65	0,4475	300	0,2575
90	0,400	360	0,2350
120	0,370	420	0,2210
150	0,355	480	0,2025

Table 4.

$Et_4N^{\oplus}I(OAc)_2^{\ominus}$ c_0 = mol/l ; c_0 = mol/l	0,42	0,487	0,512	0,665
0,53	$5,3.10^{-5}$ sec^{-1}			
0,73			$4,6.10^{-5}$ sec^{-1}	
0,97				$4,7.10^{-5}$ sec^{-1}
1.46		$6,4.10^{-5}$ sec^{-1}		

stirred at room temp for 2 hr, and the resulting brown soln allowed to stand overnight. Dry ether (300 ml) was added to the yellowish-brown soln and the mixture was cooled to 0°, the crystalline product filtered off, rapidly washed with dry ether (2×75 ml) and immediately dried in vacuum over P_2O_5, yield: 27 g (92%) m.p.: 132–134 (dec) from dry chloroform-dry ether. ($C_{12}H_{26}INO_4$, M.w.: 375.26. Found: C, 38.28; H, 6.87; I, 33.75. Calc. C, 38.41; H, 6.98; I, 33.82%). ^{1}H NMR ($CDCl_3$) δ: 1,61 t CH_3 12H; 1.95 s, CH_3CO 6H; 3.5 q, CH_2 8H.

The oil, obtained from the chloroform–ether mother liquor after evaporations of the solvent *in vacuo*, was washed with water (20 ml) dried over $CaCl_2$, and distilled at 15 mm Hg, yield: 15 g (92%) iodobenzene, b.p.: 69–70°, identical (IR) with an authentic sample.

trans-1-Acetoxy-2-iodocyclohexane

(a) A mixture of **9** (20 g; 53 mmol), cyclohexene (5.4 ml; 53 mmol) and chloroform (40 ml) was allowed to stand for 24 hr at room temp washed with aqueous (40 ml) $NaHSO_3$ (3 g) and water (2×40 ml), dried ($CaCl_2$) and evaporated in vacuum. The residue (13.3 g; 92%) was distilled at 2 mm Hg, yield: 11.6 g (82%), b.p.: 61–62°. The product identical (IR, ^{1}H NMR) with an authentic sample.[24]

(b) A mixture of I_2 (12.7 g; 50 mmol), silver acetate (8.3 g; 50 mmol) and dry ether (50 ml) was stirred for 1 hr, the resulting AgI was filtered off, washed with dry ether (2×10 ml). Cyclohexene (5.1 ml; 50 mmol) was added to the filtrate. After standing for 10 min at room temp, the mixture was shaken with aqueous (60 ml) $NaHSO_3$ (5 g), and water (2×40 ml), dried over $CaCl_2$, and the solvent was evaporated in vacuum. The residue was distilled at 2 mm Hg. b.p.: 61–62°, yield: 6.7 g (50%). The product proved identical (IR, ^{1}H NMR) with an authentic sample described in lit.[24]

9 does not react with acenaphthylene and O-acetyl-cholesterol in chloroform solution.

Diethyl acetoxy-malonate

A mixture of **9** (27 g; 72 mmol), diethyl malonate (11 ml; 72 mmol) and chloroform (50 ml) was allowed to stand at room temp for 45 min. After 10 min, tetraethylammonium iodide (8 g; 46%) started to separate. The mixture was cooled to 0°, and the salt was filtered off. The filtrate was washed with aqueous (50 ml) $NaHSO_3$ (5 g), and water (2×25 ml) and dried ($CaCl_2$). The solvent was evaporated in vacuum. The residue (13 g = 82%) was distilled at 15 mm Hg, b.p.: 136–138°, yield: 8.5 g (54%). The product proved identical (IR, ^{1}H NMR) with an authentic sample.[25]

Ethyl α-acetoxy acetoacetate

A mixture of **9** (20 g; 53 mmol), ethyl acetoacetate (6.75 ml; 53 mmol) and chloroform was allowed to stand with cooling in water. After 5 min a ppt started to form. The mixture was allowed to stand overnight, and the tetraethylammonium iodide (11.9 g; 85%) was filtered off. The filtrate was washed with chloroform (2×10 ml), dried ($CaCl_2$) ride, and the solvent was evaporated. The residue (8 g; 96%) was distilled at 10 mm Hg, b.p.: 58–59°, yield: 3.8 g (46%). The product proved identical (IR, ^{1}H NMR) with an authentic sample.[26]

1,1-*Diacetoxy-acetophenone*

A mixture of **9** (40 g; 106 mmol), acetophenone (6.2 ml; 53 mmol) and chloroform (60 ml) was allowed to stand with cooling in water. After 10 min tetraethylammonium iodide started to separate. The mixture was refluxed for 1 hr, cooled to 0°, the tetraethylammonium iodide (13 g; 48%) was filtered off, and washed with chloroform. The filtrate was washed with aqueous (180 ml) $NaHSO_3$ (6 g) and with water (2×60 ml), and dried ($CaCl_2$). The residue (11 g = 88%), obtained after the evaporation of the solvent, was distilled at 2 mm Hg, b.p.: 96–98°, yield: 6.75 g (54%). The product crystallized on cooling and was recrystallized from 75 ml heptane: 5.4 g (43%), m.p.: 54–55°. It proved identical (IR, ^{1}H NMR) with an authentic sample.[27]

Diethyl n-butyl-iodomalonate

A mixture of **9** (20 g; 53 mmol), diethyl butylmalonate (11.5 g; 53 mmol) and chloroform (40 ml) was refluxed for 1 hr or was allowed to stand for 24 hr at room temp. No ppt was formed. The mixture was diluted with chloroform (20 ml), washed with aqueous (40 ml) $NaHSO_3$ (3 g) and with water (2×40 ml), and dried ($CaCl_2$). The solvent was evaporated and the residue (18 g; 99%) was distilled at 1.5 mm Hg, b.p.: 76–78°, yield: 12.8 g (70%). ($C_{11}H_{19}IO_4$, M.w.: 342.18. Found: C, 39.09; H, 5.73. Calc. C, 38.71; H, 5.60%). ^{1}H NMR δ: 0.9–2.3 m, 15H; 4.25 q, 4H.

3 - *Methylthio* - 1,4 - *diphenyl* - Δ^2 - 1,2,4 - *triazolin* - 5 - *one* (**11**)

A mixture of **9** (12 g; 31.9 mmol), **6** (10 g; 25.3 mmol) and chloroform (50 ml) was allowed to stand for 15 min, with cooling in water, diluted with chloroform (40 ml), washed with a mixture of $NaHSO_3$ (5 g), AcOH (5 ml) and water (50 ml), then with water (2×20 ml), and dried ($CaCl_2$). The solvent was evaporated. The residue was dissolved in pentane (30 ml), the mixture evaporated to dryness and the residue (7.5 g; 99%) recrystallized from heptane (100 ml), yield: 4.9 g (68%), m.p.: 101–102°. ($C_{15}H_{13}N_3SO$, M.w.: 282.34. Found: N, 14.63; S, 11.44. Calc.: N, 14.83; S, 11.32%). ^{1}H NMR δ: 2.55 s, SCH_3 3H; 7.2–7.5 m aromatic-H 8H; 8.1 m aromatic-H 2H.

4-Hydroxy-3,5-diiodo-benzaldehyde

A mixture of **9** (20 g; 53 mmol), 4-hydroxybenzaldehyde (3.55 g; 25 mmol) and chloroform (100 ml) was allowed to stand

for a day. The mixture was evaporated to dryness in vacuum. A soln of $NaHSO_3$ (6 g), conc HCl (5 ml) and water (60 ml) was added to the residue. The resulting colourless product was filtered off, washed with water (2 × 30 ml) and dried in air at 80°, yield: 8.2 g (88%), m.p.: 203–204° (from AcOH). The product proved identical (IR; ^1H NMR: δ 8.1 s, aromatic H; 9.6 s, CHO in DMSO-d_6) with the authentic sample.[28]

Oxidation of secondary alcohols to ketones

Mixture of **9** (20 g; 53 mmol), the secondary alcohol (53 mmol) and chloroform (120 ml) were allowed to stand for 24 hr. In some cases the violet crystals of tetraethylammonium triiodide (m.p.: 139–140°; $C_{10}H_{20}I_3N$; m.w.: 535.03; Calc.: I, 71.17. Found: I, 72.20) separated were filtered off and washed with chloroform (2 × 10 ml). The filtrate was washed with a mixture of $NaHSO_3$ (8 g), AcOH (10 ml) and water (60 ml), then with water (2 × 20 ml), and dried over $CaCl_2$. After evaporation of the solvent, the respective ketones were obtained; they proved identical with the product described in the literature.

1,3-*Dimethyl-2-propylbenzimidazolium iodide* (**12**)

A mixture of N,N'-dimethyl-*o*-phenylenediamine (11 g; 80.8 mmol), butyric chloride (8.4 ml; 80.8 mmol) and dioxane (100 ml) was refluxed for 20 min and evaporated in vacuum. The residue was dissolved in water (50 ml); aqueous (160 ml) KI (40 g) was added and the soln was cooled to 0°. The resulting product was washed with a small amount of water, and dried in air at 80°, yield: 15.5 g (61%). After recrystallization from a mixture of EtOH (100 ml) and water (10 ml), yield: 13.5 g, m.p.: 230–232°. ($C_{12}H_{17}N_2I$, M.w.: 316.20. Found: C, 45.51; H, 5.38; N, 8.47. Calc. C, 45.58; H, 5.42; N, 8.86%). ^1H NMR (TFA) δ: 0.8 t, γ-CH_3 3H; 1,6β-CH_2 sextet 2H; 2.95 t, α-CH_2 2H; 3.75 s, NCH_3 6H; 7.45 s aromatic-H 4H.

2 - (1-*Hydroxypropyl*) - 1,3 - *dimethyl* - *benzimidazolium iodide* (**14**)

A mixture of **12** (12 g; 38 mmol), dry dimethylformamide (80 ml) and sodium hydride (80% suspension in mineral oil, 2 g ~80 mmol) was stirred for 30 min at room temp, cooled to 0°, filtered and the insoluble material washed with DMF (2 × 25 ml). Then combined filtrates were cooled to −45°. Dibenzoyl peroxide (9.7 g; 40 mmol) was added in small portions with stirring. Stirring was continued for further 20 min at −45°. The mixture was then allowed to warm up to 0°; it was stirred for 20 min at this temp. and poured into aqueous (150 ml) $NaHSO_3$ (10 g) and KI (50 g). Water (300 ml) was added and the organic material extracted with CH_2Cl_2 (3 × 100 ml). The combined CH_2Cl_2 solns were washed with water (2 × 100 ml), evaporated, then evaporated again with CH_2Cl_2 (100 ml). The residue was taken up in ether (100 ml), cooled to 0°, the crystallized product was filtered off and dissolved in dry MeOH (50 ml). A soln of NaOMe (2.16 g; 40 mmol) in dry MeOH (30 ml) was added, and the mixture allowed to stand overnight, and acidified with AcOH (5 ml). Ether (400 ml) was added, and the mixture allowed to stand at 0°. The crystalline product was filtered off, washed with ether, and recrystallized from EtOH (15 ml), yield: 1.1 g (8.7%), m.p.: 175–176°.

The mixture did not contain propanal in detectable quantity. ($C_{12}H_{17}N_2IO$, M.w.: 332.40. Found: N, 7.96; I, 38.53. Calc. N, 8.43; I, 38.21%). ^1H NMR (DMSO-d_6) δ: 1.05 t, γ-CH_3 3H; 2.0 m, $-CH_2$ 2H; 4.20 s, NCH_3 6H; 5.35 m, OH 1H; 6.40 d, α-CH 1H $J = 4$ Hz; 7.7–8.15 m aromatic H 4H.

5 - [(1 - N,N' - *Dietoxycarbonylhydrazino)ethyl*] - 3 - *methylthio* - 1,4 - *diphenyl* - 1,2,4 - *triazolium iodide* (**15a**)

A mixture of **2a** (5 g; 11.8 mmol) diethyl azodicarboxylate (2.3 ml; 14.7 mmol) and dry DMF (20 ml) was kept for 20 min at 100°, poured into a mixture of $NaHSO_3$ (3 g), KI (15 g), AcOH (5 ml) and water (100 ml), and cooled to 0°. The resulting solid (6.1 g) was filtered off, dried in vacuum over P_2O_5, and recrystallized from a mixture of EtOH (15 ml) and water (15 ml), yield: 4.0 g (57%), m.p.: 195–196° dec. ($C_{23}H_{28}N_5ISO_4$, M.w.: 5.97.48. (Found: N, 11.78; I, 21.70. Calc. N, 11.72; I, 21.24%). ^1H NMR ($CDCl_3$) δ: 1.20 and 1.22 t, O-CH_2-CH_3 3H and 3H; 1.50 d, CH_3 3H; 2.65 s, SCH_3 3H; 4.10 and 4.12 q, $-O-CH_2-CH_3$ 2H and 2H; 5.60 q, CH_3-CH- 1H; 7.5–7.7 m aromatic-H 6H; 8.1–8.4 m aromatic-H 4H.

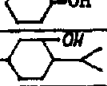
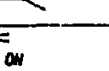
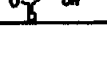
5 - [(1 - N,N' - *Diethoxycarbonylhydrazino)propyl*] - 3 - (*methylthio*) - 1,4 - *diphenyl* - 1,2,4 - *triazolium iodide* (**15b**)

A mixture of **2b** (5 g; 11.4 mmol), diethylazodicarboxylate (2.66 ml; 12 mmol) and dry DMF (20 ml) was allowed to react and worked up as described for the preparation of **15a**. The crude product (6.9 g) was recrystallised from a mixture of EtOH (40 ml) and water (10 ml); the pure product was collected after being allowed to stand for 1 day at −10°, yield: 5.5 g (79%), m.p.: 206–207°C, dec. ($C_{24}H_{30}IN_5SO_4$, M.w.: 611.51. Found: N, 11.30; I. 20.75%). ^1H NMR ($CDCl_3$) δ: 1.05 t, CH_3 3H; 1.30 and 1.32 t, $-O-CH_2-CH_3$ 3H and 3H; 1.85 q, CH_2 2H; 2.55 s, SCH_3 3H; 4.20 and 4.22 q, $-O-CH_2-CH_3$ 2H and 2H; 5.3 m, CH 1H; 7.1–7.7 m aromatic-H 10H.

3 - (*Methylthio*) - 1,4 - *diphenyl* - 1,2,4 - *triazolium bromide* (**20**)

Compound **1** (200 g; 778 mmol) was refluxed with formic acid (98–100%, 400 ml; 10 mol) for 8 hr, the mixture poured into aqueous (3000 ml) KBr (800 g; 6.7 mol) and refluxed for a few min. On cooling to 0°, an oily substance separated, which slowly crystallised. It was filtered off, washed with water (2 × 200 ml), dried in vacuum at 100° and recrystallised from EtOH (225 ml), yield: 210 g (76%), m.p.: 210–212°. ($C_{15}H_{14}N_3SBr$, M.w.: 348.27. Found: N, 12.17; Br, 22.92. Calc. N, 12.07; Br, 22.95%). ^1H NMR

Table 5.

Secondary alcohols	Ketones	Yield %	m.p. (b.p.) C°	Identification	References
$CH_3-\underset{OH}{CH}-CH-CH_3$	$CH-CO-CH-CH_3$	81	(117)	2,4-DNH	29
meso $Ph-\underset{OH}{CH}-\underset{OH}{CH}-Ph$	$Ph-CH-\underset{O}{C}-Ph$ (OH)	81	132–133		30
	PhCH = O	13	237 (2,4-DNH)	2,4-DNH	31
$Ph-\underset{OH}{CH}-\underset{O}{C}-Ph$	Ph-CO-CO-Ph	86	93–94		30
		90	(155–156)		29
		76	(208–211)		29
		46	2,4-DNH: 241–242	2,4-DNH	32

($CDCl_3$) δ: 2.85 s, SCH_3 3H; 7.45–7.6 m, aromatic H 6H; 7.8–8.0 m, 2H and 8.25–8.45 m, 2H aromatic o-H; 12.4 s, CH 1H (this last signal in DMSO-d_6 appears at 11.45).

3 - (*Methylthio*) - 1,4 - *diphenyl* - 1,2,4 - *triazolium tribromide* (**21**)

To a mixture of **20** (50 g; 143.5 mmol) and chloroform (150 ml) was added within a few mins to a mixture of bromide (7.7 ml; 150 mmol) and chloroform (150 ml) with stirring and cooling with water. The resulting yellow crystals were filtered off, washed with chloroform (2 × 50 ml) and with ether (2 × 100 ml) and dried in air, yield: 69 g (85%), m.p.: 146–147°, orange yellow crystals.

The product was be purified by dissolving in cold DMF, adding an 1:3 chloroform–ether mixture, and cooling the mixture to 0°. ($C_{15}H_{14}N_3Br_3S$, M.w.: 508.11. Found: N, 7.83; S, 6.81; Br, 47.69. Calc. N, 8.27; S, 6.31; Br, 47.19%). ^1H NMR (DMSO-d_6) δ: 2.75 s, SCH_3 3H; 7.6–8.0 m, aromatic H 10H; 11.20 s, CH 1H.

5 - *Bromo* - 3 - (*methylthio*) - 1,4 - *diphenyl* - 1,2,4 - *triazolium bromide* (**16**)

To a mixture of **21** (47 g; 92.5 mmol) and chloroform (dry, 150 ml) dry triethylamine (15 ml; 109 mmol) was added dropwise within 5 min cooling with ice and with stirring.

The resulting white ppt was filtered off, washed with chloroform (2 × 30 ml) and ether (2 × 100 ml), and dried in air, yield: 30 g (76%), m.p.: 226–227°. The product was pure enough for the following reactions. It can be purified by precipitation with ether from its TFA soln.

From the chloroform filtrate of the crude triethylammonium bromide was obtained, 66% yield by adding 300 ml ether. ($C_{15}H_{13}N_3SBr_2$, M.w.: 427.18. Found: N, 9.71; Br, 37.40. Calc. N, 9.84; Br, 37.42%). ^1H NMR (TFA) δ: 2.75 s, SCH_3 3H; 7.2 s, aromatic-H 10H.

3 - *Methylthio* - 1,4 - *diphenyl* - 5 - (*propylimino*) - Δ^2 - 1,2,4 - *triazoline* (**17a**)

To a mixture of **16** (20 g; 46.8 mmol), triethylamine (dry, 7 ml; 50 mmol) and chloroform (abs 100 ml) n-propylamine (3.85 ml; 46.8 mmol) was added dropwise with stirring. The mixture was stirred at 0° for 10 min. The resulting homogenous soln was washed with 1 N NaOH (2 × 50 ml) and water (2 × 30 ml) and evaporated to dryness in vacuum. The residue was dissolved in dichloromethane (75 ml), the solvent evaporated again; this procedure was repeated with pentane (75 ml). The resulting oil crystallised on cooling, yield: 13.9 g (91%), m.p.: 91°. Recrystallised from heptane (75 ml), yield: 12.1 g (80%), m.p.: 91°. ($C_{18}H_{20}N_4S$, M.w.: 324.44. Found: N, 17.09. Calc. N, 17.27%). ^1H NMR ($CDCl_3$) δ: 0.75 t, γ-CH_3 3H; 1.4 quintet, β-CH_2 2H; 2.55 s, SCH_3 3H; 2.75 t, α-CH_2 2H; 7.0–7.5 m aromatic-H 8H; 8.1 d aromatic-H 2H J = 8 Hz.

The following derivatives were prepared analogously:

5 - (*Benzylimino*) - 3 - methylthio - 1,4 - diphenyl - Δ^2 - 1,2,4 - triazoline (**17c**), yield 93%, m.p.: 121–122° from cyclohexane. ($C_{22}H_{20}N_4S$, M.w.: 372.48. Found: C, 71.14; H, 5.49; N, 15.06; S, 8.94. Calc. C, 70.94; H, 5.41; N, 15.04; S, 8.61%). ^1H NMR ($CDCl_3$) δ: 2.55 s, SCH_3 3H; 4.1 s, CH_2 2H; 7.1–7.4 m, aromatic H 8H; 7.4 s, benzyl aromatic H 5H; 8.1 d, aromatic H 2H.

5 - (*Isopropylimino*) - 3 - methylthio - 1,4 - diphenyl - Δ^2 - 1,2,4 - triazoline (**17g**), yield: 92%, m.p.: 130° from heptane. ($C_{18}H_{20}N_4S$, M.w.: 324.44. Found: C, 66.78; H, 6.20; N, 17.25; S, 10.00. Calc. C, 66.63; H, 6.21; N, 17.27; S, 9.88%). ^1H NMR ($CDCl_3$) δ: 0.90 d $(CH_3)_2CH$ 6H; 2.45 s, SCH_3 3H; 3.3 heptet CH 1H; 7.0–7.5 aromatic H 8H; 8.1 d, aromatic o-H 2H.

5 - (*Tetrahydrofurfurylimino*) - 3 - methylthio - 1,4 - diphenyl-2 - 1,2,4 - triazoline (**17e**), yield 99%, m.p.: 91°. ($C_{20}H_{22}N_4S$, M.w.: 350.48. Found: N, 16.01. Calc. N, 15.99%). ^1H NMR ($CDCl_3$) δ: 1.75 m, 4H; 2.45 s, SCH_3 3H; 2.95 m, 2H; 3.7 m, 3H; 7.3–7.45 m aromatic-H 8H; 8.1 d aromatic-H 2H.

3 - *Methylthio* - 3 - *morpholino* - 1,4 - *diphenyl* - 1,2,4 - *triazolium bromide* (**22**)

A mixture of **16** (5 g; 11.7 mmol) morpholine (2 ml; 23 mmol) and chloroform (30 ml) was stirred for a few minutes. Heat was evolved and a clear soln formed. This was cooled to 0°, and the resulting crystalline morpholine hydrochloride (m.p.: 212°) filtered off. The chloroform soln was washed with water (2 × 20 ml), dried over $MgSO_4$, and evaporated to dryness. The oily residue was triturated with ether (50 ml), whereby it turned into crystals which were filtered and dried in air at 80°, yield: 3.1 g (61%), m.p.: 262–264° from water. ($C_{19}H_{21}N_4OSBr$, M.w.: 433.38. Found: N, 12.73; S, 7.22. Calc. N, 12.93; S, 7.40%). ^1H NMR δ: 2.55 s, SCH_3 3H; 3.1–3.45 m, 8H; 7.5–7.7 m aromatic H 6H; 8.1–8.3 aromatic o-H 4H.

5 - *Imino* - 3 - *methylthio* - 1,4 - *diphenyl* - Δ^2 - 1,2,4 - *triazoline* (**19**)

A mixture of **16** (30 g; 70.2 mmol), ammonium hydroxide (28%, 100 ml) and EtOH (100 ml) was stirred at 0° for 20 min, diluted with ether (150 ml) and allowed to stand in a refrigerator over night. The resulting crystalline product was filtered off washed with water and dried in vacuum over P_2O_5, yield: 19 g (96%) after recrystallisation from heptane (300 ml), yield: 13 g (66%), m.p.: 92–93°. ($C_{15}H_{14}N_4S$, M.w.: Found: N, 19.59; S, 11.35. Calc. N, 19.84; S, 11.36%). ^1H NMR ($CDCl_3$) δ: 2.50 s, SCH_3 3H; 4.75 s, NH 1H; 7.3–7.5 m aromatic H 8H; 8.1 d aromatic o-H 2H;

5 - [1 - (*N,N'-Diethoxycarbonylhydrazino*) - *propyl* - *imino*] - 3 - *methylthio* - 1,4 - *diphenyl* - Δ^2 - 1,2,4 - *trizoline* (**18a**)

A mixture of **17a** (5 g; 15.5 mmol) 95% diethylazodicarboxylate (3 g; 17.2 mmol)[33] and chloroform was refluxed for 2 hr, evaporated to dryness in vacuum. Pentane (30 ml) was added to the residue and distilled off. The residue was taken up in warm hexane (30 ml) and the soln allowed to cool. The crystalline product was filtered off, washed with pentane and dried in air, yield: 7.6 g (89%), m.p.: 151°. Recrystallisation from a mixture of benzene (25 ml) and hexane (50 ml) (69% recovery) did not change the m.p. ($C_{24}H_{30}N_6O_4S$, M.w.: 498.59, Found: C, 57.92; H, 6.21; N, 16.90; S, 6.89. Calc. C, 57.81; H.6.06; N, 16.86; S, 6.43%). ^1H NMR ($CDCl_3$) δ: 0.50 t, $-CH_3$ 4H; 1.20 t, CH_3 6H; 1.8 m, $-CH_2$ 2H; 4.15 q, CH_2 4H; 5.2 and 6.4 m, CH and NH 1H and 1H; 7.3–7.5 m aromatic-H 8H; 8.1 d aromatic o-H 2H, J = 8 Hz.

Acid hydrolysis of **18a**

A mixture of **18a** (3 g; 6.0 mmol), conc H_2SO_4 (3 ml) and water (50 ml) was subjected to steam-distillation. The distillate (about 60 ml) was cooled with ice. 6 - (2 - Aminophenyl) - 3 - methylthio - 1,2,4 - triazolin - 5(2H)one (1.9 g; 8 mmol)[22] and AcOH (2 ml) were added, and the mixture was stirred for 30 min at room temp. The resulting red needles were filtered off, washed with MeOH (2 × 10 ml) and ether (2 × 50 ml), yield: 1.6 g (97%). Rapid recrystallisation from DMF gave 0.9 g (54%) 6 - propyl - 6.7 - dihydro - 3 - methylthio - [1,2,4]triazino - [1,6-c]quinazolin - 5 - ium - 1 - olate, which proved identical (IR, ^1H NMR) with an authentic sample.[22,23]

When the decomposition was performed in HClaq, **19** and N,N'-(diethyoxycarbonyl)-hydrazine were isolated:

A mixture of **18a** (4 g; 8.0 mmol), conc HCl (10 ml) and water (50 ml) was refluxed for 30 min and evaporated to dryness in vacuum. The residue was recrystallised from water (10 ml) to yield 1.05 g (74%) of N,N'-(diethoxycarbonyl)hydrazine, identical (IR, mixed m.p.) with the product described.[33]

The filtrate of this product was diluted with water (30 ml), made alkaline with 40% NaOH (pH 13) and, extracted with dichloromethane (3 × 30 ml). The combined organic phases were washed with water (2 × 30 ml) and evaporated to dryness. The residue was taken up in dichloromethane and, after evaporation of the solvent, recrystallised from heptane (50 ml), yield: 1.1 g (48%) of **19**, identical (m.p., mixed m.p., IR) with the product obtained as described above.

Decanal

A mixture of **16** (20 g; 46.8 mmol), dry triethylamine (7 ml; 50 mmol), decylamine (7.36 g; 46.8 mmol) and chloroform (100 ml) was stirred at 0° for 20 min, washed with 1 N NaOH (2 × 50 ml) and water (2 × 50 ml), and evaporated to dryness in vacuum. The residue was taken up in dichloromethane (75 ml), evaporated again to dryness and refluxed for 2 hr with 95% diethyl azodicarboxylate (10.95 g; 60 mmol)[33] in chloroform (100 ml). After cooling, the soln was washed with a mixture of $NaHSO_3$ (3.5 g; 20 mmol), 1 N NaOH (20 ml) and water (80 ml), then with water (2 × 100 ml), and evaporated to dryness. A mixture of conc. H_2SO_4 (15 ml) and water (100 ml) was added to the red oily residue and the mixture subjected to steam-distillation. The distillate (about 100 ml) was extracted with ether (60 ml and 2 × 30 ml), the ether extract was washed with 5% $NaHCO_3$aq (2 × 30 ml) and water (2 × 30 ml), dried over $CaCl_2$, and evaporated to dryness. Distillation of the residue (5.2 g; 71%) furnished 4.2 g (57%) decanal, b.p.: 206–208°, lit b.p.: 208°.[19]

Identification

A mixture of the above aldehyde (4.2 g; 26.8 mmol), 6 - (2 - aminophenyl) - 3 - (methylthio) - 1,2,4 - triazin - 5(2H) - one 6 - nonyl - 6, t - dihydro - 3 - methylthio - [1, 2, 4] triazino [1, 6-c] quinazolin - 5 - ium - 1 - date (6.4 g; 27 mmol)[22] and MeOH (30 ml) was refluxed for a few min, and the resulting red crystal needles filtered off, yield: 2.7 g (87%), m.p.: 154–155° (from isopropanol). ($C_{20}H_{28}N_4OS$, M.w.: 372.52. Found: C, 64.18; H, 7.64. Calc. C, 64.48; H. 7.58%).

In the same way as described for decanal, *benzaldehyde* (identified in the form of its 2,4-dinitrophenylhydrazone),[31] was obtained from benzylamine in 94% yield, *phenylacetaldehyde* identified in the form of its 2,4-dinitrophenylhydrazone,[31] from 2-phenylethylamine in 41% yield, and the *tetrahydrofurfural* from tetrahidrofurfurilamin 17% yield; this aldehyde was isolated from the steam-distillate in the form of 6,7 - dihydro - 3 - (methylthio) - 6 - (tetrahydrofurfuryl) (([1,2,4]triazino - [1,6 - c]quinazolin - 5 - ium - 1 - olate, m.p.: 210–211° from DMF. ($C_{15}H_{16}N_4SO_4$, M.w.: 316.36. Found: C, 57.30; H, 5.04; S, 9.86. Calc. C, 56.94; H, 5.10; S, 10.13%).

5,5 - *Dimethoxy* - 3 - *methylthio* - 1,4 - *diphenyl* - Δ^2 - 1,2,4 - *triazoline* (**23**)

(a) A mixture of **16** (20 g; 46.8 mmol), NaOMe (5.4 g; 100 mmol) and dry MeOH (80 ml) was stirred for 15 min at 0°, and allowed to stand at 0° overnight. The resulting product was filtered off, washed with MeOH (at 0°, 2 × 10 ml), and dried in air, yield after recrystallization from heptane 10 g (65%), white cubes, m.p.: 110–111°. ($C_{17}H_{19}N_3O_2S$, M.w.: 329.41. Found: C, 61.36; H, 5.46; N, 13.01; S, 9.40. Calc. C, 61.98; H, 5.81; N, 12.76; S, 9.73%). ^1H NMR ($CDCl_3$) δ: 2.55 s, SCH_3 3H; 3.20 s, CH_3O 6H; 6.9–7.45 m aromatic H 10H.

(b) A mixture of **22** (7 g; 16.1 mmol), NaOMe (1.35 g; 25 mmol) and dry MeOH (70 ml) was stirred for 30 min at 0°, then allowed to stand in a refrigerator overnight. The product was filtered off and washed with MeOH (at 0°, 2 × 5 ml), yield: 3.5 g (66%), and IR spectrum. The product proved identical (m.p., mixed m.p., IR) with the product prepared according to section (a).

3 - *Methylthio* - 1,4 - *diphenyl* - Δ^2 - 1,2,4 - *triazoline* - 5 - *on* (**11**)

(a) A mixture of **23** (9 g; 27.3 mmol), phenylacetic acid (3.68 g; 27 mmol) and heptane (20 ml) was refluxed for 30 min. After cooling, the product was filtered off and washed with heptane (2 × 5 ml), yield: 3.5 g (88%), m.p.: 104°. The product proved identical (mixed m.p., IR) with a a sample of **11**, obtained by the reaction of **6** with **9** as described.

The heptane filtrate was evaporated to dryness in vacuum, and the residue was distilled to obtain methylphenylacetate (3.5 g; 86%) b.p.: 216–220°. Which proved identical (IR) with an authentic sample.

(b) A mixture of **16** (10 g; 23.4 mmol), benzoic acid (5.7 g; 46.7 mmol), dry chloroform (50 ml) and dry triethylamine (6.7 ml; 48 mmol) was stirred. Heat was evolved and a clean soln formed which was allowed to stand overnight, diluted with ether (150 ml), and cooled to 0°. The resulting triethylamine hydrobromide (8.2 g; 94%, m.p.: 253°) was filtered off, and the filtrate was evaporated to dryness in vacuum. The residue was stirred with pentane (3 × 50 ml) and the insoluble product was filtered off, and recrystallisated from heptane, yield: 4.1 g (61%) of **11**, which proved identical (m.p., mixed m.p., IR) with the product obtained as described in section (a).

The pentane filtrate was evaporated to obtain 2.8 g (53%) benzoic anhydride (b.p.: 348–350°, which proved identical (IR, b.p.) with an authentic sample.

(c) A mixture of **16** (10 g; 23.4 mmol), benzoic acid (2.68 g; 22 mmol), dry triethylamine (6.7 ml; 48 mmol) and dry chloroform (50 ml) was stirred for 5 min at 0°; aniline (2.4 ml; 24 mmol) was added, and stirring was continued for 15 min at 0°. The mixture was evaporated to dryness in vacuum; the residue was triturated with water (2 × 50 ml) and dissolved in acetone (40 ml). Water (10 ml) was added and the mixture allowed to stand at 0°. The resulting product was filtered off, washed with water and dried in air at 80°, yield: 2.7 g (62%) of benzanilide, m.p.: 161–162° (from acetone) which identical (mixed m.p., IR) with an authentic sample.

The aqueous-acetonic filtrate was diluted with water (200 ml) and extracted with dichloromethane (2 × 50 ml). The dichloromethane phase was washed with water (2 × 50 ml), dried over $CaCl_2$ and evaporated to dryness in vacuum. The residue was recrystallised from heptane (150 ml) to obtain: 4.9 g (79%) of **11**, m.p.: 101°, which was identical (IR) with the sample obtained according to selection (a).

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