Tetrahedron Vol. 31, pp. 1391 to 1398. Pergamon Press 1975. Printed in Great Britain

FASCINATING PROBLEMS IN ORGANIC REACTION MECHANISMS-VII[1]

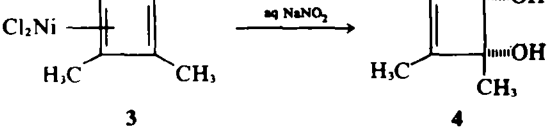
NOVEL SODIUM NITRITE-AQUEOUS ACID CIS-HYDROXYLATION REACTION†

S. RANGANATHAN* and S. K. KAR
Department of Chemistry, Indian Institute of Technology, Kanpur-16, U.P., India

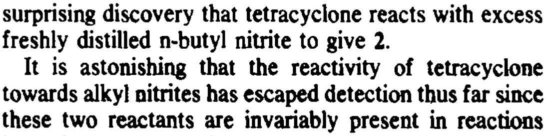
(*Received in UK* 20 *November* 1974; *Accepted for publication* 12 *December* 1974)

Abstract—Tetraphenylcyclopentadienone 1 is transformed in 85% yields to the cis diol 2 with sodium nitrite-aqueous acetic acid, under conditions usually employed for deamination. This change, and clean cis-hydroxylation of tetramethyl cyclobutadiene constitute notable examples of cis-hydroxylation with sodium nitrite-aqueous acid. Reactions of tetracyclone with dinitrogen trioxide, dinitrogen tetroxide, dinitrogen pentoxide, nitrous acid and nitric acid show that nitric acid is the reagent involved in cis-hydroxylation. Unknown facets related to the chemistry of oxides of nitrogen, the most significant being the existence of the olefin + $N_2O_3 \rightleftharpoons$ adduct equilibrium have been revealed, and the chemistry of the adducts has been studied. Of a variety of substrates examined, only dienes respond to the sodium nitrite-aqueous acid reagent. The minimum requirements for the reaction are that the substrate be a good diene and that the initially formed [4 + 2] adduct shall decompose by a C–N bond rupture. A similar sequence explains the fascinating transformation of tetracyclone to pentaphenyl pyrrole in boiling nitrobenzene.

This paper presents, inter alia, work related to the rationalization of the following two fascinating transformations:



1   85% 2



3   4

The genesis of the 1→2 cis-hydroxylation, under conditions employed for de-amination, was the result of the surprising discovery that tetracyclone reacts with excess freshly distilled n-butyl nitrite to give 2.

It is astonishing that the reactivity of tetracyclone towards alkyl nitrites has escaped detection thus far since these two reactants are invariably present in reactions involving the generation and characterisation of arynes from appropriate amino acid precursors.[2] Subsequent to our preliminary report on the 1→2 change,[3] Professor Criegee kindly informed us that tetramethylcyclobutadiene-nickel chloride complex undergoes clean cis-hydroxylation when stirred with aqueous sodium nitrite.[4] The structural assignment for 2 was confirmed by comparison with sample prepared in 31% yield by reaction of 1 with nitric acid.[5] Further, the cis assignment was confirmed by the preparation of 2 by treatment of 1 with osmium tetroxide under carefully controlled conditions. Parallel studies were then initiated to understand these arresting transformations and to explore the $NaNO_2$/aq AcOH combination as a new cis-hydroxylating agent. The former studies yielded in addition to a logical explanation of the cis-hydroxylation, several novel transformations. It has now been possible to predict the requirements for this type of cis-hydroxylation. These are unusual and only highly selective substrates satisfy the required conditions.

The reagent

The sodium nitrite-aqueous acetic acid combination could provide a variety of reagents such as nitrous acid, dinitrogen trioxide, dinitrogen tetroxide, dinitrogen pentoxide and nitric acid. Consequently a study of the reaction of tetracyclone with each of the above reagents was investigated. Such a study not only provided a rational route to the 1→2 change, but also brought to light several subtle factors associated with oxides and oxyacids of nitrogen.

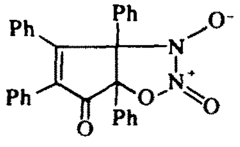
Reaction of dinitrogen trioxide with tetracyclone

At low temperatures dinitrogen trioxide has been identified as the reactive species involved in sodium nitrite/aqueous acid reactions and therefore it was considered probable that this reagent may be involved in the 1→2 change. Following this reasoning, an ice-cooled, dry, benzene solution of 1 was treated dropwise with a dry benzene solution of dinitrogen trioxide prepared by reaction of As_2O_3 and nitric acid[6] until the intense pink colour of tetracyclone was completely discharged. The reaction was extremely rapid and took only few minutes (~10 min) for completion and removal of benzene under no exclusion of moisture gave rise to the cis-diol 2 in 85% yield. However, removal of benzene under reduced pressure and rigorously dry conditions gave a colourless foamy material, m.p. 95°C(dec), assigned structure 5 on the basis of analysis, IR and molecular weight (osmometry).‡ Alternate formulations possessing a C–NO_2 linkage are considered unlikely in view of the extreme ease with which the adduct is transformed to the

---

†Respectfully dedicated to Professor T. R. Govindachari on the occasion of his sixtieth birthday.

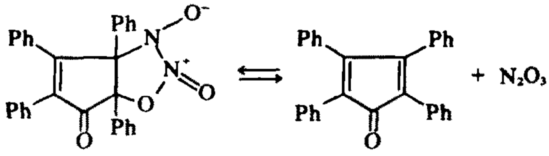
‡All spectral data are presented in Experimental.



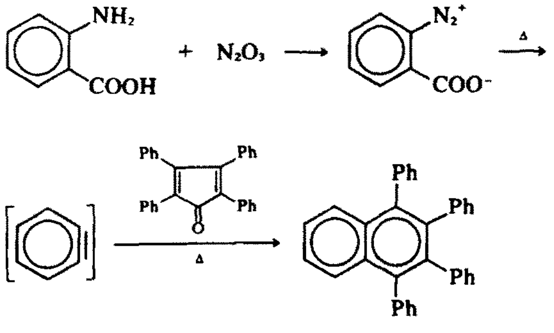
5

diol **2** as well as its ready reversal to tetracyclone and dinitrogen trioxide (vide infra).*

The adduct **5** could be transformed to the diol **2** with great ease and under a variety of conditions, such as treatment with water, aqueous acetic acid, moist dioxane and moist tetrahydrofuran. In the latter two cases a flash of the tetracyclone colour was observed. This suggested that the change **5**→**2** was not direct but proceeded through tetracyclone. This was demonstrated in a most dramatic manner by treating the adduct **5** with dry methanol. The reaction mixture at once assumed the characteristic pink colour of tetracyclone and evaporation of solvents under exclusion from moisture gave tetracyclone in quantitative yields. This unexpected reversal has no precedent. We rationalize this transformation on basis of the following equilibrium: adduct$\rightleftharpoons$tetracyclone $+ N_2O_3$. The facile reversal is in good agreement with structure **5** for the adduct. Attempts directed at further characterization of the adduct **5** were unsuccessful principally because of the extreme readiness with which it undergoes reversal. The possibility that it is a simple charge transfer complex is highly unlikely in view of lack of colour, IR spectra, and non-appearance of peaks either in the visible near IR region, or ESR signals. The lack of colour and the ESR study also excludes structures involving a nitroso grouping in the adduct **5**. A dimeric structure for the adduct **5** is also excluded on the basis of osmometric molecular weight data.† The reversal of the dinitrogen trioxide adduct was further demonstrated in a fascinating manner by treating it with anthranilic acid to produce tetraphenylnaphthalene **6** in 20% yields. This reaction is rationalized on basis of reversal of the adduct to tetracyclone, reaction of the elements of dinitrogen trioxide so produced with anthranilic acid to give o-diazonium carboxylate which in turn undergoes fragmentation to benzyne to be captured by tetracyclone to give the product **6**.



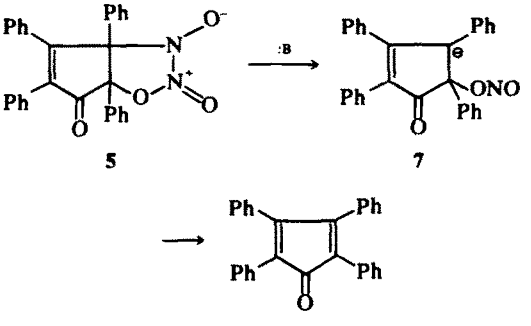
5 **1**



6

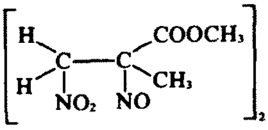
The reversal of adduct **5** to tetracyclone can also be brought about by weak bases like carbazole and skatole. In constrast, added tetracyanoethylene did not affect adduct **5**.

We rationalize that the reversal of **5** is initiated by acceptance of elements of NO^+ by any type of nucleophile present to generate the stabilized ion **7** which in turn readily loses elements of NO_2^- to give **1**:

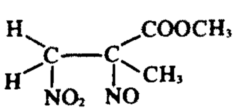


5 **7** **1**

Consequently, it would be predicted that any dinitrogen trioxide adduct which could by loss of elements of NO^+, yield a stabilized ion similar to **7** should show pronounced tendency for reversal. This was demonstrated with the only well characterized dinitrogen trioxide adduct, namely, that arising from methyl methacrylate.[7] This compound exists as a colourless dimer **8** at room temperature, with rapid monomerization to the blue **9** around 70°C:

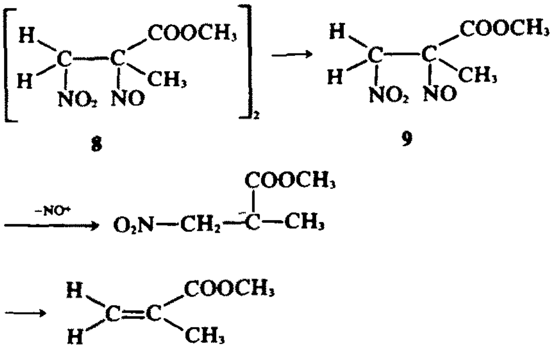


8



9

When solutions of **9** are allowed to stand at 0°C for 3–4 days methacrylate is formed (NMR). This exceptionally facile reversal is in excellent accord with the earlier rationalization:



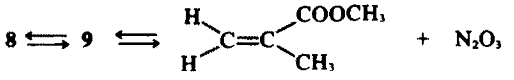
8 **9**

---

*The orientation of the N_2O_3 in adduct **5** is supported by the formation of nitro-olefin from "tricyclone" which has an unsaturated position adjacent to carbonyl.

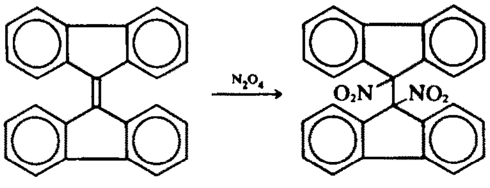
†Copious evolution of oxides of nitrogen took place on boiling a clear dry benzene solution of **5** to give a complex mixture, exhibiting a streaking TLC pattern and consisting of at least nine products.

Additionally when **9** was treated with 9,9′-difluorenylidene **10**, the dinitro compound **11**[8] was isolated in 50% yields. The formation of **11** is rationalized on the basis of reversal of **9**. The elements of dinitrogen trioxide formed at this temperature (70°C) would exist in equilibrium with other oxides of nitrogen. Compound **11** is formed by homolytic addition of dinitrogen tetroxide so produced to **10**:



$$8 \rightleftharpoons 9 \rightleftharpoons \mathrm{H_2C{=}C(CH_3)COOCH_3} + \mathrm{N_2O_3}$$

$$2\mathrm{N_2O_3} \rightleftharpoons \mathrm{N_2O_4} + 2\mathrm{NO}$$



10 **11**

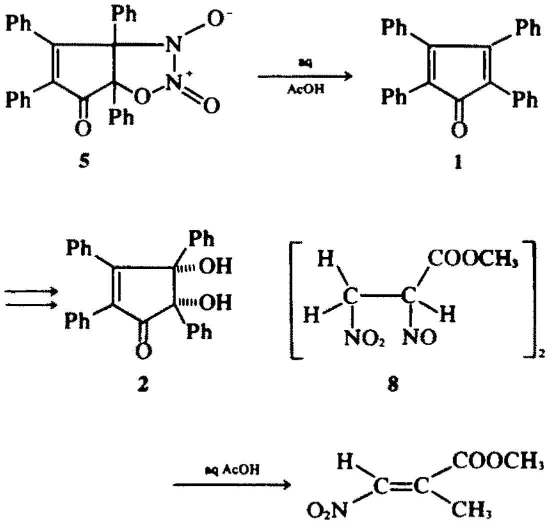
Parenthetically 9,9′-difluorenylidene **10** exhibits a pronounced tendency to add dinitrogen tetroxide as shown by the formation of **11**, even on treatment of **10** with sodium nitrite–aqueous acetic acid around 0°C. The reversal of the methyl methacrylate adduct **8** was demonstrated in a fascinating manner with tetracyclone **1** at 70°C to give cis-dibenzoyl stilbene (20%) and 2-benzoyl-3,4,5-triphenylfuran **12** (60%). The formation of these products could be rationalized on the basis of addition of dinitrogen tetroxide to **1** proceeding by two possible pathways, namely, 1,2-addition (path a) and 1,4-addition (path b) both of which have precedence.

The transformation of the 1,2-adduct to the furan takes place in an unexpected manner. The 1,4-adduct is transformed to cis dibenzoyl stilbene involving the novel extrustion of CO:

Interestingly dinitrogen tetroxide with tetracyclone at 0°C gives only cis dibenzoyl stilbene thus indicating a preference for 1,4-addition at lower temperatures (path b) (vide infra).

The reversal of methyl methacrylate dinitrogen trioxide adduct is a spontaneous process. It is most likely that, similar reversal also takes place with tetracyclone adduct **5** although the solvent assited reversal is definitely a more facile one.

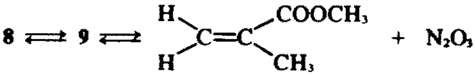
The tetracyclone adduct **5** in aqueous acetic acid yields the diol **2**, by a process involving complete reversal; in contrast the methyl methacrylate adduct **8** in aqueous acetic acid yields exclusively the nitro olefin **13** by partial elimination:



5 **1** **2** **8** **13**

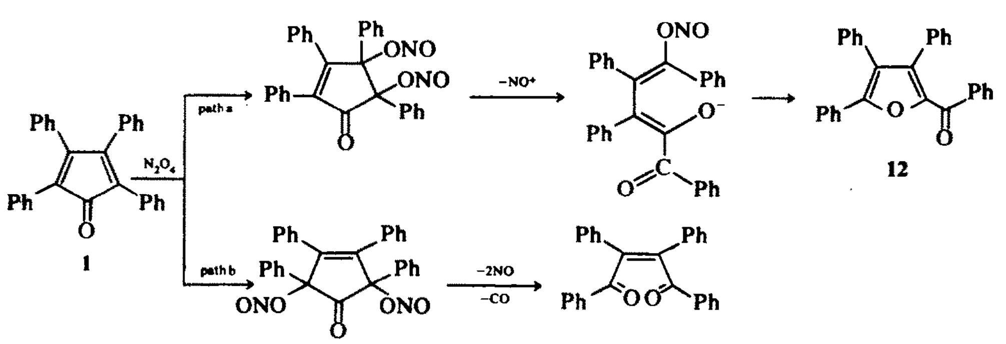
Reaction of dinitrogen tetroxide with tetracyclone

Addition of dinitrogen tetroxide[9] to tetracyclone at 0° led rapidly to a 20% yield of cis dibenzoylstilbene.



$$8 \rightleftharpoons 9 \rightleftharpoons \mathrm{H_2C{=}C(CH_3)COOCH_3} + \mathrm{N_2O_3}$$

$$2\mathrm{N_2O_3} \rightleftharpoons \mathrm{N_2O_4} + 2\mathrm{NO}$$



1 **12**

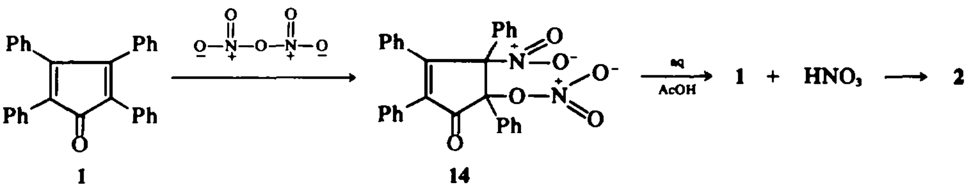
Interestingly, when the clear solution resulting from the addition of N_2O_4 to tetracyclone at 0° was refluxed for 1 hr and then worked up, a 55% yield of the stilbene was obtained and no furan could be detected. These results indicate that at 0°, N_2O_4 adds exclusively to give the 1,4-adduct, which then undergoes thermal CO-extrusion to give the stilbene.*

---

*In attempts to simulate the conditions of the methyl methacrylate adduct—tetracyclone exchange, an ice-cold dry benzene solution of dinitrogen tetroxide was injected into a dry benzene solution of tetracyclone, held at 80°, until complete decolorization. Work-up after an additional hour reflux gave a very complex mixture from which, by careful preparative TLC, cis dibenzoylstilbene (5%) and furan **12** (~1%) could be isolated.

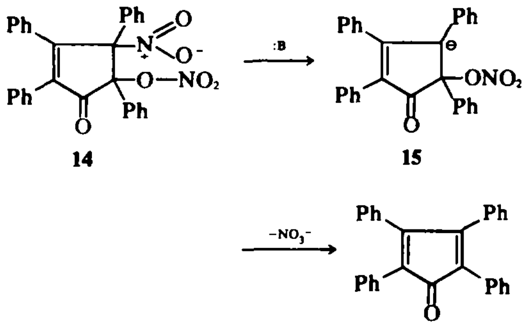
Reaction of dinitrogen pentoxide with tetracyclone

Dinitrogen pentoxide reacted with tetracyclone in a manner similar to N_2O_3. Thus, when a methylene chloride solution of N_2O_5[10] was treated with tetracyclone in methylene chloride instantaneous decolorization took place and addition of aqueous acetic acid gave diol **2** (55%). Alternatively, when the methylene chloride was evaporated under rigorous exclusion from moisture and the residual foamy, highly reactive material treated with dry methanol, reversal took place leading to 55% of tetracyclone. The dinitrogen pentoxide adduct is assigned structure **14**:



1 **14**

The reversal of dinitrogen pentoxide adduct **14** could be readily rationalized on the basis of acceptance of elements of NO_2^+ by the solvent to give **15** which then loses NO_3^- to give **1**:

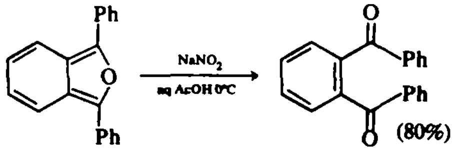


14 **15** **1**

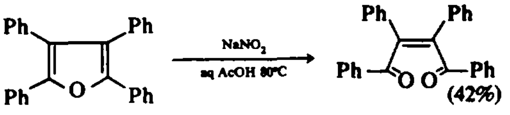
The work described thus far clearly rules out the oxides of nitrogen, namely, dinitrogen trioxide, dinitrogen tetroxide and dinitrogen pentoxide as the reagents involved in cis-hydroxylation which leaves the two oxyacids, namely, nitrous and nitric acid. Indeed it has been demonstrated that the dinitrogen trioxide and dinitrogen pentoxide additions are clearly divorced from cis hydroxylation. It was found that nitric acid, made free of nitrous acid by addition of urea is equally effective while pure nitrous acid prepared by passing aqueous sodium nitrite over an ion exchange resin at 0°C[11] reacts quite slowly with the substrates when compared to the usual conditions employed in the change **1**→**2**. Further, nitric acid reacts with all substrates that give products with $NaNO_2$/aq AcOH, although in lower yields.

Reaction of unsaturated systems with sodium nitrite aqueous acetic acid

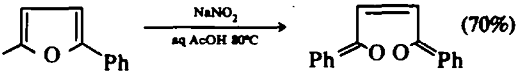
Of the several systems reacted with sodium nitrite aqueous acetic acid under conditions of the **1**→**2** change, the diene systems responded quite favourably. Even amongst them a strong parallel was observed between the reactivity of the dienes and its reaction with sodium nitrite–aqueous acetic acid. Thus, 2,5-diphenylisobenzofuran **16** reacted readily with sodium nitrite aqueous acetic acid at 0° to give o-dibenzoyl benzene in 80% yields. The furans **17** and **18** reacted, although less readily, under conditions where the reagent could not be well defined to give the cis dibenzoyl olefins: A variety of olefinic systems including dihydrotetracyclone, diphenylcyclopropenone, tetraphenylethylene, cis-dibenzoylstilbene and trans-dibenzoylethylene, were found to be totally unresponsive to $NaNO_2$/aq AcOH reagent.



16



17



18

Rationalization

We conclude that the sodium nitrite–aqueous acetic acid reaction takes place through nitric acid, which is produced from nitrous acid:

$$3\,HNO_2 \rightleftharpoons HNO_3 + 2\,NO + H_2O.$$

The above process is a favourable one under conditions of sodium nitrite–aqueous acetic acid reactions[12] and the superior yields obtained with the reagent can readily be explained on the basis of sodium nitrite–aqueous acetic acid as a steady source of nitric acid, thus, avoiding unfavourable side reactions that take place with nitric acid alone.

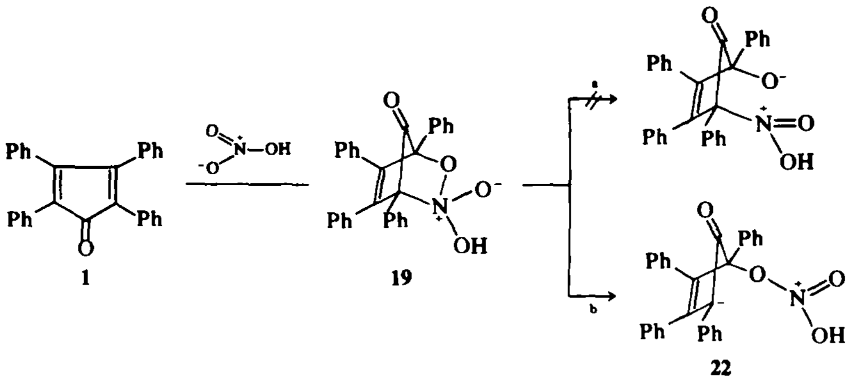
Our work[3] and that communicated by Professor Criegee,[4]* as well as that of others[5] strongly support the fact that nitric acid could readily react with powerful 1,3-diene systems.† Consequently, it is reasonable to surmise that the primary step in the interaction of the dienes with nitric acid is the formation of simple [4+2] adducts of the types **19**, **20** and **21**. The diverse possibilities that are available for the further fragmentation of these unstable intermediates are outlined below.

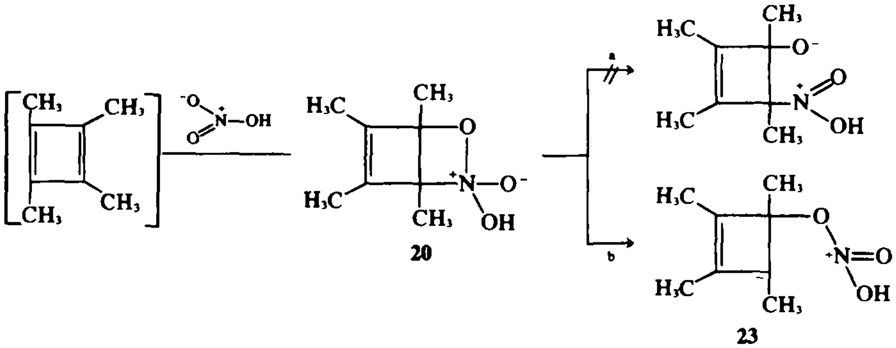
Path a leading to the N–O bond rupture is not preferred in systems **19** and **20**, both these cases preferring path b, leading to a C–N bond rupture. In the case of **19** the C–N

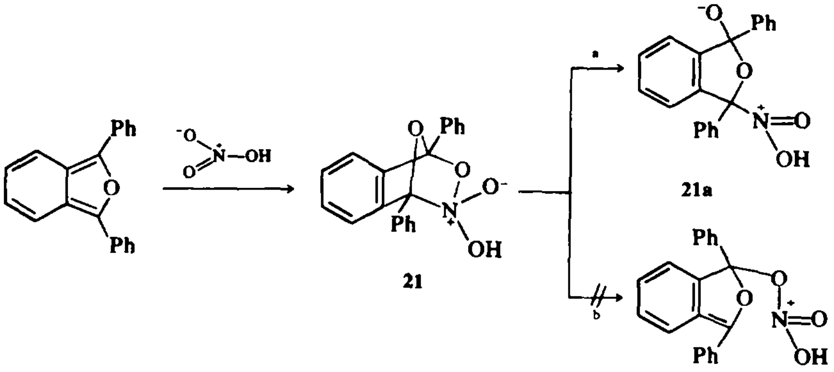
---

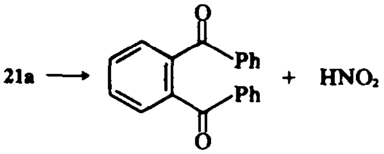
*Tetracyclone undergoes cis hydroxylation with aqueous $NiCl_2$ and $NaNO_2$.

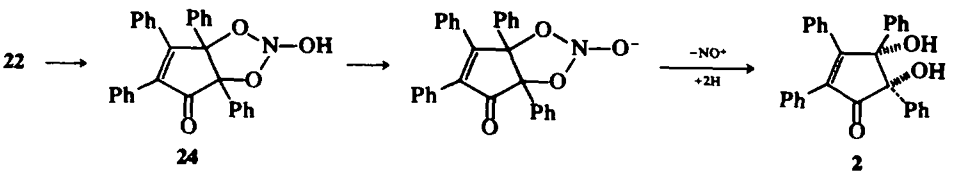
†Indeed nitric acid mimics ozone in the transformation of furans to cis acyl olefins.

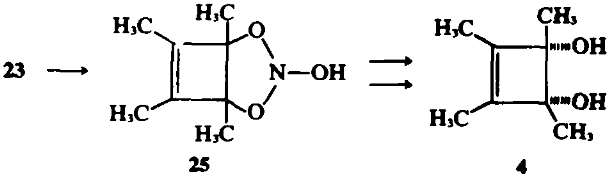

1
19
22
a
b


20
23
a
b


21
21a
a
b


21a
+ HNO₂


22
24
−NO⁺
+2H
2

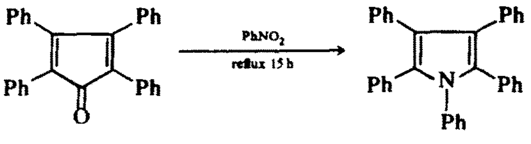

23
25
4

bond rupture leads to a highly stabilized ion. In the case of isobenzofuran, the oxygen bridge in adduct **21** makes N–O bond rupture overwhelmingly possible, since this mode makes the ready extrusion of elements of nitrous acid possible, leading to products. Thus the N–O bond rupture could be predicted to lead to cis olefinic diketones. In contrast to this, the cases where the C–N bond is ruptured the stabilized nucleophilic systems created, namely **22** and **23** undergo facile intramolecular addition to produce intermediates **24** and **25**. Species **24** and **25** are precisely those which could, in principle, arise from [4 + 2] addition involving nitric acid and the dienes, the former acting as a 1,3-dipolar species. But the present work makes such a direct addition unlikely, particularly in view of the inertness of diverse olefinic systems to either sodium nitrite–aqueous acetic acid or nitric acid. The transformation of **24** and **25** to the cis diols can be most readily rationalized on the basis of loss of elements of NO^+ from the corresponding conjugate bases.

The unusual sodium nitrite–aqueous acetic acid cis-hydroxylation is explained on basis of generation of nitrous acid, equilibration to nitric acid, [4 + 2] addition, C–N bond rupture, recyclization and extrusion of elements of NO^+ from the cyclized adduct. The minimum requirement for observance of cis-hydroxylation are that the substrate be a good diene and that the initially formed [4 + 2] adduct should preponderantly decompose by a C–N bond rupture. These requirements, as can be readily seen, restrict drastically the types of systems which could undergo cis-hydroxylation.

At the present time the $NaNO_2$/aq AcOH cis-hydroxylation appears to be a rare reaction. It is certain, however, that further work based on the conclusions presented here would bring out, as in the case of benzoin condensation, many additional examples.

The participation of the nitro function in thermal cycloaddition reactions is very rare. Nevertheless, in the event that the $NaNO_2$/aq AcOH cis-hydroxylation proceeds through steps outlined above, it should be expected that tetracyclone would react with other reagents possessing the nitro function. This is indeed so.



1

The above reaction discovered by Dilthey[13] and reinvestigated by us[14] has many similarities with the cis-hydroxylation. The most striking observation is the formation of furan **12** from tetracyclone and nitrobenzene and *p*-cyanonitrobenzene in 6% and 20% yields respectively. The **1**→**12** change can be rationalized via intermediates **26** and **27**, which are similar to **19** and **22** envisaged for the cis hydroxylation.

EXPERIMENTAL

M.ps and boiling points are uncorrected. Unless otherwise stated, IR spectra were recorded on a Perkin-Elmer model-137 instrument, and NMR spectra on a Varian A-60 instrument using TMS as internal standard. Silica gel G (Stahl) was used for thin layer chromatography and column chromatography with silica gel (BDH).

Reaction of tetracyclone with excess n-butyl nitrite. Isolation of cis-2,3-dihydroxy-2,3,4,5-tetraphenylcyclopent-4-en-1-one **2**

To a stirred solution of tetracyclone[15] (0·5 g, 1·3 mmole), in 20 ml benzene, freshly distilled n-butyl nitrite (1·3 g, 13 mmole) was added. The mixture was stirred overnight at room temperature, and solvents evaporated under reduced pressure. The residue on crystallization from benzene gave 0·38 g (70%) of a white crystalline compound, m.p. 190–191°C (dec) identified as *cis*-2,3-dihydroxy-2,3,4,5-tetraphenylcyclopent-4-en-1-one 2 on the basis of mixed m.p. (190–191°C dec) and other comparisons with an authentic sample (vide infra).

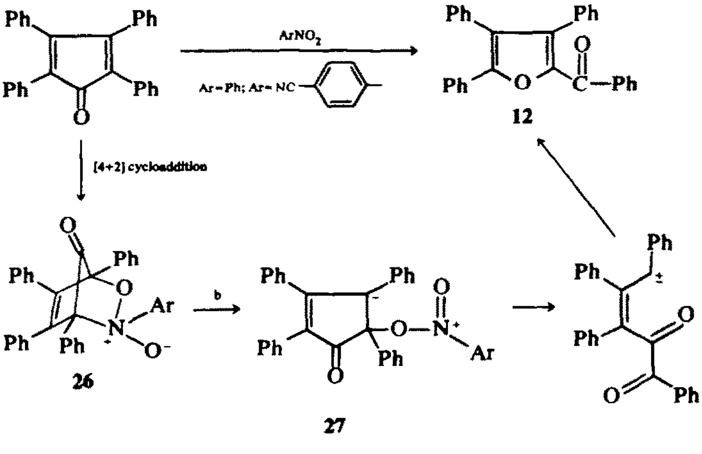
(Calc. for $C_{29}H_{22}O_3$: C, 83·25; H, 5·26. Found: C, 83·52; H, 4·98%.) IR: ν_{max} (KBr): 3400 (OH); 1698 (C=O) cm^{-1}. NMR: δ ($CDCl_3$): 7·2 (aromatic protons).

Reaction of tetracyclone with sodium nitrite and aqueous acetic acid, A standard procedure for the preparation of **2**

A stirred solution of tetracyclone (0·5 g, 1·3 mmole) in 10 ml benzene was treated with acetic acid–water (3:2, 5 ml) and the mixture was cooled to 0°C. Solid sodium nitrite (0·5 g, 7 mmole) was introduced over a period of 15 minutes below 5°C. The colourless reaction mixture was stirred for an additional 30 min, the layers separated, the organic layer washed several times with water, dried ($MgSO_4$) and solvents evaporated under reduced pressure. The residue on crystallization from benzene gave 0·46 g (85%) of **2**, m.p. 190–191°C (dec).

Reaction of tetracyclone with osmium tetroxide: isolation of authentic **2**

A solution of tetracyclone (0·5 g, 1·3 mmole) in 20 ml ice-cooled dry ether was treated with osmium tetroxide (0·33 g, 1·3 mmole) and pyridine (1 ml) and the mixture was stirred at room temperature for 72 hr. The insoluble complex was decomposed with mannitol (5 g) in 10% aqueous KOH (20 ml) and stirring continued for 12 hr. The reaction mixture was extracted with



methylene chloride, the organic layer washed with water, dried ($MgSO_4$) and solvents were evaporated under reduced pressure. The residue on crystallization from benzene gave 0·34 g (63%) of a white crystalline compound, m.p. 190–191°C (dec.), whose m.p. was not depressed by admixture with **2** (m.p., 190–191°C dec) prepared from tetracyclone and nitric acid.[5]

Reaction of tetracyclone with sodium nitrite in aqueous nickel chloride: isolation of **2**

A stirred solution of tetracyclone (0·384 g, 1 mmole), in 5 ml benzene was mixed with $NiCl_2 \cdot 6H_2O$ in water (2·35 g, 10 mmole, 20 ml, pH 6) and cooled to 0°C. To this, solid sodium nitrite (2 g, 28 mmole) was added over a period of 24 hr. Stirring continued for 48 hr, maintaining the temperature below 10°C, when no tetracyclone remained (by TLC). Then 10 ml of benzene was added, the organic layer separated, washed several times with water, dried ($MgSO_4$) and solvents evaporated under reduced pressure. The residue on crystallization from benzene gave 0·250 g (60%) of **2**, m.p. 191–192°C (dec) which was identical in all respects to authentic **2**. Tetracyclone was recovered unchanged in the absence of added nickel chloride.

Reaction of tetracyclone with dinitrogen trioxide in the presence of aqueous acetic acid: isolation of **2**

A stirred solution of tetracyclone (0·2 g, 0·52 mmole) in 5 ml benzene was treated with acetic acid-water (3:2, 5 ml) and mixture cooled to 0°C. A dilute dry benzene solution of dinitrogen trioxide was added dropwise until decolorization was complete (10 ml). The clear solution was stirred for additional 30 min, the organic layer separated, washed several times with water, dried ($MgSO_4$) and solvents evaporated under reduced pressure. The residue on crystallization from benzene gave 0·18 g (85%) of **2**, m.p. 192–193°C (dec).

Reaction of tetracyclone with dinitrogen trioxide in benzene under anhydrous conditions: isolation of the adduct **5**

A stirred and ice cooled solution of tetracyclone (0·5 g, 1·3 mmole) is 10 ml dry benzene was treated dropwise with a dry benzene solution of dinitrogen trioxide until decolorization was complete. The solvent was removed in vacuo and without heating under rigorously dry conditions to give 0·5 g (83%) of a noncrystalline solid **5**, m.p. 95°C (dec). (Calc. for $C_{29}H_{20}N_2O_4$: N, 6·08. Found: N, 6·01%). Molecular weight (osomometry): 450 ± 15; calculated: 460. IR: ν_{max}(KBr): 1750 (C=O); 1540, 1335 cm^{-1} and also present 3500 (OH); 1698 (C=O) cm^{-1} due to decomposition of **5** to **2**.

Reaction of tetracyclone with dinitrogen trioxide in dry benzene. Reversal with absolute methanol

A stirred solution of tetracyclone (0·384 g, 1 mmole) in 10 ml dry benzene was treated dropwise with a dilute dry benzene solution of dinitrogen trioxide until decolorization was complete, keeping the temperature below 5°C. Absolute methanol (30 ml) was then added immediately to the reaction mixture and stirring continued for 4 hr maintaining the temperature below 5°C. Then solvents were removed under reduced pressure under anhydrous condition to give 0·29 g of tetracyclone (TLC) (75%) which on crystallization from benzene/ethanol gave 0·2 g (55%) of tetracyclone, m.p. 223°C.

Reaction of tetracyclone with dinitrogen trioxide under anhydrous conditions and then exchange with anthranilic acid: isolation of tetraphenylnaphthalene **6**

A stirred solution of tetracyclone (0·384 g, 1 mmole) in 20 ml dry methylene chloride was treated dropwise with a dilute solution of dinitrogen trioxide in dry methylene chloride until decolorization was complete. Then anthranilic acid (0·15 g, 1 mmole) in dry tetrahydrofuran (10 ml) was added to the reaction mixture in one lot and stirring continued at room temperature. Tetracyclone colour reappeared soon after the addition. Diglyme (10 ml) was added and the mixture was heated to remove all the methylene chloride and tetrahydrofuran. Then it was refluxed at 160°C for 2–3 hr. Tetracyclone colour disappeared again. Solvents were removed under reduced pressure. TLC examination of the crude product indicated presence of tetraphenylnaphthalene (by comparison with authentic tetraphenylnaphthalene). The crude product was then chromatographed over silicic acid using benzene/hexane 1:1 and benzene as eluent. A pale yellow compound 0·085 g (20%), m.p. 169°C, identified as tetraphenylnaphthalene by comparison with authentic sample,[2] was obtained.

Preparation of dinitrogen trioxide adduct of methyl methacrylate[7]*: isolation of dimer* **8**, *monomer* **9** *and demonstration of reversal*

A stirred solution of methyl methacrylate (5 g, 50 mmole) in 10 ml ether was treated with aqueous sulphuric acid (2:3, 10 ml) and the mixture was cooled to 0°C. Solid sodium nitrite (5 g, 70 mmole) was introduced over a period of 15 min while maintaining the temperature below 5°C. The reaction mixture was stirred for additional 30 min when some white solid began to separate. The mixture was quickly filtered, the white residue was washed with cold ether (10 ml) and then with cold water (20 ml) and dried to yield 3·5 g (40%) of **8**, m.p. 100–110°C.[7] (Calc. for $[C_5H_8O_5N_2]_2$: C, 34·1; H, 4·6; N, 15·9. Found: C, 34·0; H, 4·56; N, 15·18%). IR: ν_{max} (KBr): 1740 (C=O); 1545, 1360 cm^{-1}. NMR: δ (CD_3COCD_3): 1·45 (saturated CH_3), 3·88 (methylene). On warming in benzene the dimer yields the blue monomer. NMR: δ (CD_3COCD_3): 1·46 (saturated CH_3), 5·37 (methylene). Blue solutions on standing at 0° for 3–4 days are quantitatively transformed to methyl methacrylate. NMR: δ ($CDCl_3$): 1·93 (q, $-CH_3$), 3·73 (s, $-OCH_3$), 5·54 (1H), 6·08 (1H).

Reaction of 9,9′-difluorenylidene with dinitrogen trioxide adduct of methyl methacrylate: isolation of 9,9′-dinitro-9,9′-difluorenyl **11**

A stirred solution of 9,9′-difluorenylidene prepared from 9-bromofluorene[16] (0·328 g, 1 mmole) in 20 ml benzene was mixed with warm (60–70°C) benzene solution of dinitrogen trioxide adduct of methyl methacrylate (0·342 g, ~ 2 mmole, 20 ml) under anhydrous condition and stirring continued at 60–70°C for 2 hr and then at room temperature for 24 hr. Solvents were removed under reduced pressure and the residue was crystallized from ether to give 0·21 g (50%) of 9,9′-dinitro-9,9′-difluorenyl, m.p. 183–184°C identified on the basis of comparison with an authentic sample.[8] (Calc. for $C_{26}H_{16}N_2O_4$: C, 74·28; H, 3·8; N, 6·69. Found: C, 74·18; H, 3·56; N, 6·62%). IR: ν_{max} (KBr): 1540 (asymmetric, $-NO_2$), 1335 (asymmetric, $-NO_2$) cm^{-1}.

Reaction of tetracyclone with dinitrogen trioxide adduct of methyl methacrylate in dry benzene: isolation of cis-dibenzoyl-stilbene and 2-benzoyl-3,4,5-triphenylfuran **12**

A stirred solution of tetracyclone (0·384 g, 1 mmole) in 10 ml benzene was mixed with warm (60–70°C) benzene solution of dinitrogen trioxide adduct of methyl methacrylate (0·352 g, 2 mmole, 10 ml). Stirring was continued for 30 min at 60–70°C when tetracyclone colour disappeared. Solvents were removed under reduced pressure and the residue on crystallization from ether gave 0·24 g (60%) of white needles, m.p. 164–166°C identified as 2-benzoyl-3,4,5-triphenylfuran **12** on the basis of comparison with authentic sample.[17] The filtrate was evaporated and the residue on crystallization from ethanol gave 0·046 g (20%) of pale yellow needles, m.p. 213–14°C, identified as cis dibenzoyl stilbene on the basis of comparison with authentic sample.[18] (Calc. for **12** ($C_{29}H_{20}O_2$): C, 87·0; H, 5·0. Found: C, 86·91; H, 5·1%).

Reaction of tetracyclone with dinitrogen tetroxide

(a) *Addition at 0°C and work-up: isolation of cis-dibenzoyl-stilbene in low yields.* To a stirred ice cooled CCl_4 solution of tetracyclone (0·384 g, 1 mmole, 20 ml) was added dropwise a dilute CCl_4 solution of N_2O_4[9] till decolorization was complete (~10 ml). After 0·5 hr stirring, the mixture was poured into ice-water, the organic layer separated, washed several times with water, dried ($MgSO_4$) and evaporated. The gummy residue on crystallization from ethanol gave 0·75 g (20%) of cis-dibenzoylstilbene, m.p. 213–14°C.

(b) *Addition at 0°C and work-up after reflux: isolation of cis-dibenzoyl stilbene in enhanced yields.* To a stirred ice cooled CCl_4 solution of tetracyclone (0·384 g, 1 mmole, 20 ml) was added in drops a dilute solution of N_2O_4 in CCl_4 till decolorization was complete. The solution was allowed to warm to room temperature and refluxed for 1 hr. Solvents were evaporated and the residue on standing crystallized. Recrystallization from ethanol gave 0·212 g (55%) of cis dibenzoylethylene, m.p. 211–12°C.

Reaction of methyl methacrylate with sodium nitrite-aqueous acetic acid: isolation of the nitro-olefin 13

A stirred solution of methyl methacrylate (5 g, 50 mmole) in 10 ml benzene was treated with acetic acid: water (3:2, 20 ml) and the mixture was cooled to 0°C. Solid sodium nitrite (5 g, 70 mmole) was gradually introduced over a period of 15 min while maintaining the temperature below 5°C. The reaction mixture was stirred for additional 6 hr the layers were separated, the organic layer was washed several times with water and dried ($MgSO_4$) and solvents evaporated. The residue on distillation gave 3·6 g (45%) of an yellow liquid b.p. 90°C (4 mm) identified as methyl 2-methyl-3-nitroacrylate 13.[7] (Calc. for $C_5H_7NO_4$: C, 41·37; H, 4·82; N, 9·64. Found: C, 41·4, H, 4·9; N, 9·4%). IR: ν_{max} ($CHCl_3$): 1725 (C=O); 1640 (C=C); 1540 (asymmetric, $-NO_2$), 1350 (symmetric, $-NO_2$) cm^{-1}. NMR: δ (CCl_4): 2·2 (d, $-CH_3$), 3·8 (s, $-OCH_3$), 7·6 (q, -H).

Reaction of dinitrogen trioxide adduct of methyl methyacrylate with aqueous acetic acid in benzene: isolation of the nitro-olefin 13

A warm solution of dinitrogen trioxide adduct of methylmethacrylate (1·76 g, 10 mmole) in 30 ml benzene was stirred at room temperature with acetic acid: water (3:2, 10 ml) for 24 hr, then poured into water, organic layer separated, washed with water, dried ($MgSO_4$) and solvent removed. The residue on distillation gave 0·72 g (50%) of 13, b.p. 90°C (4 mm).

Reaction of methylmethacrylate with dinitrogen trioxide followed by aqueous work-up: isolation of the nitro-olefin 13

A stirred benzene solution of methyl methacrylate (5 g, 50 mmole, 10 ml) was treated with excess benzene solution of dinitrogen trioxide and the mixture was cooled to 0°C. Stirring continued for 6 hr and the reaction mixture was diluted with cold water (50 ml). The layers were separated, the organic layer was washed several times with water and dried ($MgSO_4$) and solvents evaporated. The residual liquid on distillation gave 4·2 g (53%) of 13, b.p. 90°C (4 mm).

Reaction of tetracyclone with dinitrogen pentoxide in methylene chloride: isolation of 2

To a stirred ice cooled solution of tetracyclone (0·384 g, 1 mmole) in 10 ml methylene chloride was added dropwise a dilute methylene chloride solution of dinitrogen pentoxide[10] until decolorization was complete. The mixture was stirred for another 30 min and was then poured into ice cold water. The organic layer was separated, washed several times with water dried ($MgSO_4$) and solvents removed. The residue on crystallization from benzene gave 0·23 g (55%) of 2, m.p. 191–192°C (dec.).

Reaction of 2,5-diphenylisobenzofuran with sodium nitrite and aqueous acetic acid: isolation of o-dibenzoyl benzene

A stirred ice cooled solution of 2,5-diphenylisobenzofuran (0·270 g, 1 mmole) benzene (20 ml) was treated with aqueous acetic acid (1:3, 5 ml). To this, solid sodium nitrite (0·5 g, 7 mmole) was added over a period of 15 min while maintaining the temperature below 5°C. Stirring was continued for another 30 min after which the mixture was diluted with water (30 ml), the organic layer separated, washed several times with water, dried ($MgSO_4$) and solvents removed. The residue on crystallization from ether gave 0·23 g (80%) of o-dibenzoyl-benzene, m.p. 146–148°C.

Reaction of 2,5-diphenylisobenzofuran with dinitrogen trioxide followed by aqueous work-up: isolation of o-dibenzoyl benzene

A stirred ice cooled solution of 2,5-diphenylisobenzofuran (0·27 g, 1 mmole), in 20 ml benzene was treated dropwise with a dilute benzene solution of dinitrogen trioxide (10 ml) until the yellow colour of 2,5-diphenylisobenzofuran disappeared. Stirring was continued for another 30 min at the end of which the reaction mixture was diluted with cold water (30 ml). The organic layer was separated, washed several times with water, dried ($MgSO_4$) and the solvents removed under reduced pressure. The residue on crystallization from ether gave 0·23 g (80%) of o-dibenzoyl benzene, m.p. 146–148°C.

Reaction of tetracyclone with sodium nitrate and conc H_2SO_4 *in dark: isolation of diol* 2

Under protection from light, a stirred solution of tetracyclone (0·384 g, 1 mmole) in 20 ml methylene chloride was treated with solid sodium nitrate (2 g, 24 mmole) and cooled to 0°C. Conc H_2SO_4 (98%) (5 ml) was added and stirring continued for 15 hr while maintaining the temperature at 0°C. At the end of 15 hr when the tetracyclone colour disappeared (TLC) the reaction mixture was diluted with ice cold water (50 ml), organic layer separated washed with water then with saturated aqueous $NaHCO_3$ and finally with water, dried ($MgSO_4$) and solvents evaporated under reduced pressure. The residue on crystallization from benzene gave 0·2 g (48%) of 2, m.p. 192–194°C (dec).

Reaction of tetracyclone with HNO_3 *in dioxane in the presence of urea at room temperature: isolation of diol* 2

A solution of tetracyclone in dioxane (0·5 g, 1·3 mmole, 10 ml) was first treated with 20 mg of urea and then with conc HNO_3 (70%) (2 ml). The solution was kept in the dark at room temperature with occasional shaking. Tetracyclone colour began to fade after 7 days and at the end of 15 days no tetracyclone was left (TLC). The solution was diluted with ice cold water (50 ml) and extracted with benzene (20 ml). The organic layer was washed first with water and then with aqueous $NaHCO_3$ and finally with water, dried ($MgSO_4$) and solvents removed under reduced pressure. The residue on crystallization from benzene gave 0·2 g (60%) of 2, m.p. 190–192°C (dec).

Acknowledgements—We are grateful to Professor R. Criegee, Institute fur organische Chemie, Universitat Karlsruhe, for suggestions and to Dr. Nityanand, CDRI, Lucknow, for providing NMR facilities. Financial assistance from CSIR, Delhi and Lady Tata Memorial Trust, Bombay is gratefully acknowledged.

REFERENCES

[1] Paper 6, S. Ranganathan and H. Raman, *Tetrahedron* **30**, 63 (1974).

[2] L. Friedman and F. M. Logullo, *J. Am. Chem. Soc.* **85**, 1549 (1963); R. W. Franck and K. Yanagi, *J. Am. Chem. Soc.* **90**, 5814 (1968); B. Baigrie, J. I. G. Cadogan, J. R. Mitchell, A. K. Robertson and J. T. Sharp, *J. C.S. Perkin I* 2563 (1972).

[3] S. Ranganathan and S. K. Kar, *J. Org. Chem.* **35**, 3962 (1970).

[4] R. Criegee and G. Schroder, *Ann. Chem.* **623**, 1 (1959).

[5] P. Yates and G. H. Stout, *J. Am. Chem. Soc.* **76**, 5110 (1954).

[6] G. Brauer, *Preparative Anorganischen Chemie*, Vol. I, p. 438. Ferdinand Enke Verlag, Stuttgart (1960).

[7] H. Shechter and D. E. Ley, *Chem. and Ind.* 535 (1955).

[8] C. D. Nenitzescu, *Chem. Ber.* **62**, 2669 (1929).

[9] A. G. Brook, *J. Chem. Soc.* 5040 (1952).

[10] T. E. Stevens and W. D. Emmons, *J. Am. Chem. Soc.* **79**, 6008 (1957).

[11] C. S. Scanley, *Ibid.* **85**, 3888 (1963).

[12] K. Jones, *Comprehensive Inorganic Chemistry* (Edited by A. F. Trotman-Dickinson), p. 372. Pergamon, Oxford (1973); T. A. Turney and G. A. Wright, *Chem. Rev.* **59**, 497 (1959).

[13] W. Dilthey, G. Hurtig and H. Passing, *Chem. Abstr.* **35**, 1784 (1941).

[14] S. Ranganathan and S. K. Kar, *Tetrahedron Letters* 1855 (1971).

[15] J. R. Johnson and O. Grummitt, *Organic Syntheses* (Edited by E. C. Horning), Coll. Vol. III, p. 506. Wiley, New York (1955).

[16] J. R. Sampey and E. E. Reid, *J. Am. Chem. Soc.* **69**, 234 (1947).

[17] F. Quint, R. Putter and W. Dilthey, *Chem. Ber.* **71**, 356 (1938).

[18] N. M. Bikales and E. I. Becker, *J. Org. Chem.* **21**, 1405 (1956).