N-Bromosuccinimide-Induced Dimethyl Sulfoxide Oxidation of Acetylenes[1]

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The addition of less than 2 mol equiv. of *N*-bromosuccinimide (NBS) to a solution of diphenylacetylene in anhydrous dimethylsulfoxide (DMSO) leads to the formation of benzil in near-quantitative yield at room temperature. Under the same conditions stilbene gives the dibromo adduct. The conditions for this novel oxidation *of an acetylene* have been examined in some detail and it has been established that *anhydrous DMSO* must be employed as the *solvent* and that NBS is uniquely able to induce the oxidation. Preliminary studies indicate that alkyl aryl, dialkyl, and terminal acetylenes are converted to the corresponding α-dicarbonyl compounds, and that diphenylbutadiyne is oxidized to diphenyltetraketone. Optimum conditions for these latter oxidations have not yet been established.

L'addition à la température ordinaire de *N*-bromosuccinimide (NBS), moins de 2 équivalents, à une solution de diphénylacétylène dans du diméthylsulfoxyde (DMSO) conduit à la formation de benzil avec un rendement presque quantitatif. Dans les mêmes conditions, le stilbène conduit au dérivé dibromé. Les conditions conduisant à cette nouvelle oxydation *d'un acétylène* ont été examinées en détail et il a été établi que du *DMSO anhydre* doit être utilisé comme *solvant* et que seul le NBS peut induire l'oxydation. Des études préliminaires indiquent que les arylalkylacétylènes, dialkylacétylènes, et acétylènes vrais sont transformés en composés carbonylés-α correspondants et que le diphénylbutadiyne est oxydé en diphényltetracétone. Les conditions optimales pour ces dernières oxydations n'ont pas encore été établies.

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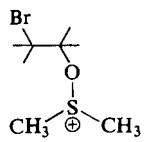
The combination of an *N*-haloamide or imide and an aqueous medium is often employed to convert an alcohol into a ketone or an olefin into a halohydrin (1). Hypohalous acid, formed *in situ* by hydrolysis of the halogen source, is thought to be the oxidizing agent in most of these reactions (2). However, recent work by van Tamelen and Sharpless (3) and by Dalton and co-workers (4) indicates that the intervention of HOX is not obligatory. In aqueous glyme, *N*-bromosuccinimide (NBS) appears to effect direct transfer of positive bromine to a double bond (3); and, in the reaction of NBS with an olefin in moist dimethyl sulfoxide (DMSO), attack on the brominated cation or bromocarbonium ion is at least 95% by the DMSO (4). The bromohydrin is then produced by hydrolysis of the oxysulfonium intermediate **1**.



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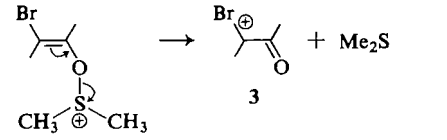
Acetylenes resemble olefins in a number of respects in their behavior towards these halogenating agents. With hypobromous acid, dibromoketones are produced (5) and, with *N*-chlorosuccinimide or NBS in alcoholic solvents, the products are dichloro (6) or dibromoketals (7). In aqueous glyme, NBS effects direct transfer of bromine to a triple bond (7). This similar behavior of olefins and of acetylenes suggested that, in DMSO, a brominated *vinyl* cation might, like its dihydro analog, be trapped by the solvent to give **2**, an unsaturated oxysulfonium cation. In the case of **2**, however, competition may now occur between hydrolysis and either unimolecular (**2** → **3**; eq. 1) or bimolecular (**2** + DMSO → **4**; eq. 2) elimination of dimethyl sulfide. Loss of $Br^{\oplus}$ and dimethyl sulfide from **4**, formed by the reactions of **2** or **3** with DMSO, would then lead, as indicated in eq. 3, to **5**, an α-diketone, in what might be described as NBS-induced DMSO oxidation.

[1] 

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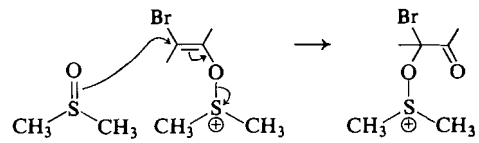
[2] 

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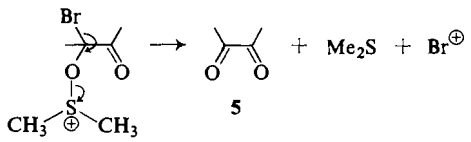
[1]Part II in the series "Aspects of Acetylene Chemistry". For Part I see ref. 34.

TABLE 1. Effect of reaction conditions on the oxidation of diphenylacetylene (tolan)

Reactant (mmol)						Recovery of products (%)	
Tolan	Halogen source	DMSO	Solvent*	Time (h)	Temperature (°C)	Benzil	Other
1.5	NBS (3.0)		DMSO	24	22	98	
1.5	NBS (3.0)		DMSO	0.5	80	92	
1.5	NBS (1.5)		DMSO	24	22	93	
1.5	NBS (0.75)		DMSO	24	22	42	58†
1.5	NBS (0.38)		DMSO	24	22	20	69†
1.5	NBS (3.0)	6.0	CH_2Cl_2	308	Reflux	<1	90–95†
1.5	NBS (3.0)	3.0	Benzene	21	Reflux	<1	98†,‡
1.5	NBS (3.0)	3.0	Dioxane	26	Reflux	1–5	56†
1.5	NBS (3.0)	20.0	Dioxane	69	Reflux	5	94†
1.5	NBS (3.0)	3.0	CCl_4	30	Reflux	0	
1.5	NBS (3.0)		DMSO-H_2O§	150	22	0	15‖
1.5	PHT¶ (3.0)		DMSO	72	22	<2	
1.5	NBA** (3.0)		DMSO	100	22	19	
1.5	Br_2 (3.0)		DMSO	48	22	0	

*Ten ml of solvent were used in each case.
†Unreacted tolan.
‡Tolan dibromide was detected in trace amounts.
§DMSO, 99.5%; H_2O, 0.5%.
‖Tolan dibromide.
¶Pyrrolidone hydrotribromide.
**N-bromoacetamide.

[3] 

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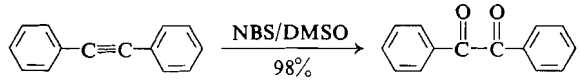
Although the scheme just depicted is intended to represent a working hypothesis rather than a mechanistic proposal, it will be noted that there are formal precedents for it in the well-known Kornblum (8) and Pfitzner–Moffatt (9) oxidations, and in the conversion of benzylamines to benzaldehydes upon diazotization in anhydrous DMSO (10). It may also be noted that oxidation of acetylenes to α-diketones has been observed previously: stearolic acid is converted to 9,10-diketostearic acid by neutral aqueous permanganate (11); and the highly strained acetylenes 3,3,6,6-tetramethyl-1-thiacycloheptyne and cyclooctyne undergo air oxidation to α-diketones (12).

Addition of NBS (0.5 g, 2.8 mmol) at room temperature to a solution of diphenylacetylene (**6**) (0.25 g, 1.4 mmol) in anhydrous DMSO (10 ml) afforded a bright yellow solution which was allowed to stand for 24 h at room temperature and then diluted with water. Chloroform extraction of the strongly acidic aqueous solution and work-up of this extract afforded benzil (**7**) *in 98% yield* (eq. 4). Repetition of the experiment for 30 min at 80° led to the formation of benzil *in 92% yield*. In contrast to these results, stilbene (**8**) reacted at room temperature with NBS in anhydrous DMSO to give the adduct meso-stilbene dibromide (**9**) (eq. 5).

Table 1 summarizes a number of experiments performed to define the conditions for the oxidation of diphenylacetylene, and the following main conclusions may be drawn: (*a*) DMSO must be utilized as the solvent since its presence in stoichiometric quantities in refluxing methylene chloride, benzene, carbon tetrachloride, or dioxane leads to only traces of benzil (*cf.* ref. 13); (*b*) NBS may function as a catalyst for the oxi-

[4] 

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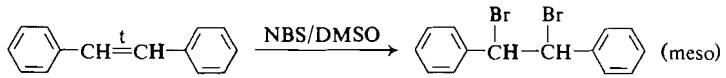
[5] 

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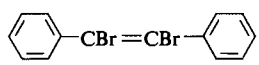
TABLE 2. Effect of reaction conditions on the oxidation of 1-phenylpropyne (**11**) in anhydrous DMSO

Reactant (mmol)		DMSO	Temperature		Composition of the reaction mixture (%)*			
11	Catalyst	(ml)	Time (h)	(°C)	**11**	**12**	**13**	**14**
4.41	A† (8.82)	20	52	20	5	21	20	21
4.43	A (4.46)	25	93	20	27	15	11	8
4.41	A (4.46)	10	45	90	14	40	22	8
4.41	A (4.46)	10	21	150	—	30	19	—
4.53‡	A (8.95)	10	49	20	Trace	12	19	17
4.74§	A (9.48)	10	70	20	0	0	0	0
4.44	B‖ (4.47)	30	701	20	27	16	—	—
4.41	B (4.52)	30	26	60	32	16	8	8
4.27	C¶ (8.70)	10	143	20	100	0	0	0

*Determined by n.m.r.
†NBS, dried but not recrystallized.
‡Calcium carbonate, 4.53 mmol, were added to the reaction mixture.
§Cyclohexene, 9.49 mmol, was added to the reaction mixture.
‖NBS, recrystallized and dried.
¶Acetic anhydride, 8.70 mmol, was substituted for the NBS. The product consisted of unreacted **11** and CH_3SCH_2OAc, the product of a Pummerer reaction of the anhydride with the solvent.

dation as implied by the above scheme; based on acetylene consumed, the ratio (mmol of diketone)/(mmol of NBS) is always greater than unity. However, because NBS is itself slowly consumed by DMSO (4), high conversions to benzil require 1–2 mol equiv of NBS per mol of acetylene; (*c*) NBS is unique in its ability to catalyze the reaction; with molecular bromine and pyrrolidone hydrotribromide (14), no diketone is produced, and with *N*-bromoacetamide the yield of benzil is only 19% after 100 h at room temperature. These findings are compatible with an initiation step for the reaction which involves direct transfer of bromine from NBS to the triple bond; (*d*) the reaction is inhibited by water; the only product formed (in a very slow reaction) in moist DMSO is diphenylacetylene dibromide (**10**).



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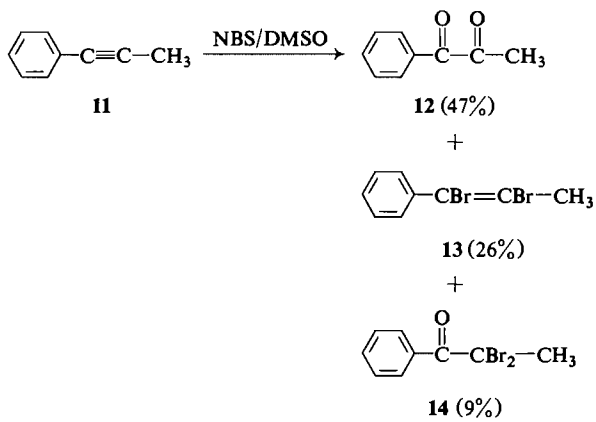
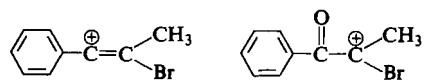
A preliminary study of the scope of the oxidation indicates that the conversion of acetylenes to α-diketones with NBS in DMSO may be a general reaction, but the optimum conditions for different types of substrates will differ from those established for **6**. The experiments summarized in Table 2 refer to the oxidation of 1-phenylpropyne (**11**) to 1-phenylpropanedione (**12**). For the conditions examined, the optimum conversion (47%) was realized with 0.4 *M* solutions containing 1 mol equiv of NBS per mol of substrate at 90°. In contrast to the oxidation of **6**, a diarylacetylene, the oxidation of **11**, an alkyl arylacetylene, produced significant quantities of bromine-containing side-products (eq. 6). These products, the dibromide **13** and the

[6]



11 **12** (47%) + **13** (26%) + **14** (9%)

dibromoketone **14**, may be considered to result from a competition for the intermediates **15** and **16**[2] between a bromine source in the medium (Br_2, HBr, NBS) (4) and the DMSO solvent. It is not at present clear why the bromine sources compete successfully for these cations when one of the substituents is an alkyl group and not when two aryl substituents are present. Oxidation of **9** in the presence of calcium carbonate (to remove HBr) did not reduce the yields of the side-products; and addition of cyclohexene to an oxidation mixture (to remove Br_2) caused the oxidation to be quenched. Replacement of the NBS by acetic anhydride led only to a Pummerer reaction of the anhydride with the solvent (15), the acetylene being recovered unchanged. We are presently examining alternatives to DMSO for the oxygen transfer step.



15 **16**

Oxidations of 2-butyne (**17**) and phenylacetylene (**18**) with NBS in anhydrous DMSO were performed at room temperature. In each case the total product was then treated with a derivatizing agent to yield biacetyl (**19**) (as the dihydrazone, see eq. 7) and phenylglyoxal (**20**) (as the di-*p*-nitrophenylhydrazone; see eq. 8), respectively. The derivatives were recovered in 20–25% yields. For these two oxidations, detailed examination of the reaction mixtures, and variation of the experimental conditions, were not performed.

It was of interest to examine the oxidation of a compound containing more than one triple bond. Polyacetylenes are readily available synthetic (16) and naturally occurring (17) compounds, and the polyketones potentially available from these substrates would be useful in several ways: base-catalyzed cyclization of the polyketone derived from a non-conjugated polyacetylene could be compared with the analogous treatment of a poly-β-ketone (18); and examination of molecular models suggests that a conjugated polyketone derived from a conjugated polyacetylene might adopt a chiral and, in favorable cases, a helical conformation (19).

[2]It has been established (5, 7) that electrophilic addition of halogen to **9** affords the vinyl cation $PhC^{\oplus}{=}CXCH_3$ preferentially.

Diphenylbutadiyne (**21**) was selected as the substrate for the preliminary study since the potential oxidation product, diphenyltetraketone (**22**) is a known compound (19, 20). Oxidation of **21**, at room temperature for 48 h or at 100° for 2 h, in DMSO containing 2 mol equiv of NBS appeared to proceed smoothly to give **22** (eq. 9). The compound was identified by its reversible color reaction with water (20, 21): red(anhydrous) ⇄ yellow(hydrate), by acid-catalyzed decarbonylation to benzil (22), and by formation of the known dioxime (20). However, although the reaction evidently proceeded smoothly, and no other product could be detected after extended reaction periods, we have been unable to crystallize the compound in either of its two forms. Both forms have been crystallized (19, 20). Consequently, although the reaction shows promise as a route to polyketones, more work is needed and is in progress.

Experimental

Melting points were determined on Fisher–Johns or Kofler hot stage m.p. apparati, and are uncorrected. The i.r. spectra were recorded on a Beckman IR 5A instrument, and calibrated against the 6.238 μ peak of polystyrene. The n.m.r. spectra were obtained on Varian A60 or T60 spectrometers as 10% solutions in chloroform-*d* or carbon tetrachloride. Tetramethylsilane was employed as an internal standard.

All solvents were dried before use by standard procedures. Dimethyl sulfoxide was refluxed over calcium hydride and then distilled under reduced pressure. It was stored in sealed bottles over 4A molecular sieves. *If the calcium hydride treatment was omitted, no oxidation took place.*

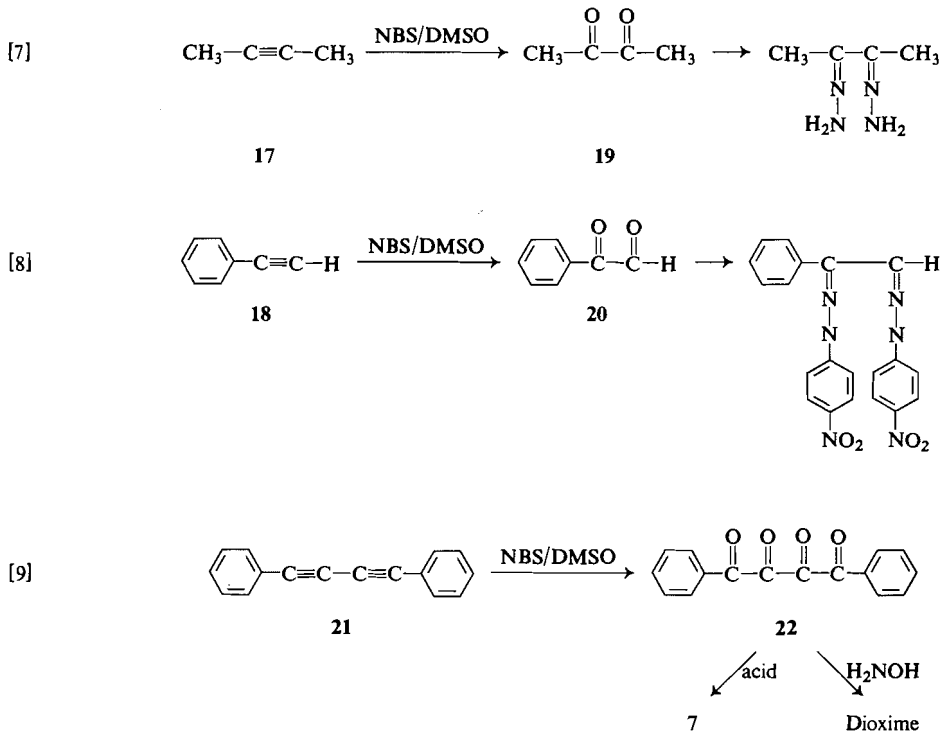
N-Bromosuccinimide was Fisher reagent grade material and was dried under reduced pressure over phosphorus pentoxide before use. Some samples, as indicated in Tables 1 and 2, were recrystallized prior to the drying procedure (23).

Diphenylacetylene was prepared from benzil by the method of ref. 24; it was purified by distillation under reduced pressure, followed by crystallization from 95% ethanol.

1-Phenylpropyne was prepared by methylation of lithium phenylacetylide in liquid ammonia (25). In the n.m.r. spectrum the methyl group of this compound appears at τ 8.02.

Diphenylbutadiyne was prepared by oxidative coupling of lithium phenylacetylide with potassium permanganate (26).

1,2-Dibromo-1,2-diphenylethylene (**10**) was prepared by bromination of diphenylacetylene. Diphenylacetylene (0.5 g, 2.8 mmol) was dissolved in chloroform (10 ml). A solution of bromine (2.8 mmol) in carbon tetrachloride was then added all at once. The color of the red solution slowly faded during a 4 h period at room temperature. Removal of the solvent then afforded a



white solid, m.p. 65–173°. This was recrystallized from absolute ethanol to give 0.6 g of **10**, m.p. 211–212° (lit. (27) m.p. 211°).

1,2-Dibromo-1-phenylpropene (**13**) was prepared by bromination of 1-phenylpropyne. The acetylene (1.1 g, 9.5 mmol) in chloroform (10 ml) was cooled in an ice-bath and a solution of bromine (1.52 g, 9.5 mmol) in chloroform (20 ml) was added dropwise with stirring. When the addition was complete the solvent was removed from the colorless solution and the residual oil distilled.

Anal. Calcd. for $C_9H_8Br_2$: C, 39.17; H, 2.90. Found: C, 39.51; H, 2.97.

In the n.m.r. spectrum, the methyl peak of this compound appears at τ 7.42.

1-Phenyl-2,2-dibromopropane-1-one (**14**) was prepared from propiophenone. The ketone (1.0 g, 7.45 mmol) and NBS (2.6 g, 14.9 mmol) were refluxed in carbon tetrachloride (20 ml) containing 2 mg of benzoyl peroxide over a 100 W Photoflood No. 2 bulb. After 10 min an orange coloration appeared in the mixture and, after an additional 8 min, the color disappeared and the reaction was complete. Filtration followed by evaporation of the solvent yielded **14** as a pale yellow oil. This oil was found to be homogeneous by t.l.c. and by n.m.r. In the n.m.r. spectrum the methyl group appears at τ 7.30. Distillation of a portion of the oil gave crystalline material, m.p. 30–31° (lit. (28) 31°). This material gave a yellow 2,4-dinitrophenylhydrazone, m.p. 266–267°.

1-Phenylpropanedione (**12**) was prepared from propiophenone by oxidation with selenium dioxide (29). In the n.m.r. spectrum the methyl group of this compound appears at τ 7.72.

Oxidation of Diphenylacetylene

Diphenylacetylene (0.25 g, 1.4 mmol) was dissolved in anhydrous DMSO. The solution was stirred and NBS (0.5 g, 2.8 mmol) was added in one portion. The solid dissolved immediately to give a bright yellow solution. There was no temperature change. After 24 h at room temperature the solution was diluted with water (60 ml), and a pale yellow solid precipitated. The solid was isolated by extraction into chloroform (the aqueous phase was found to have p*H* 2). The chloroform extract was washed successively with water and saturated sodium chloride, and was then dried ($MgSO_4$) and evaporated. The pale yellow oil (280 mg) crystallized on standing. Its i.r. spectrum was identical with that of benzil. Recrystallization from methylene chloride – petroleum ether (30–60°) afforded light yellow needles, m.p. 94.5–95.5°, undepressed on admixture with benzil.

Anal. Calcd. for $C_{14}H_{10}O_2$: C, 79.98; H, 4.79. Found: C, 79.38; H, 4.75.

The compound gave a pale orange 2,4-dinitrophenylhydrazone (2,4-DNP) derivative, m.p. 190–191°, undepressed on admixture with the 2,4-DNP derivative of benzil.

Attempted Oxidation of trans-Stilbene

trans-Stilbene (0.253 g, 1.4 mmol) and NBS (0.25 g, 1.4 mmol) were dissolved in anhydrous DMSO (5 ml). There was no temperature change, but the solution gradually developed a pale yellow color. After 24 h at room temperature the solution was diluted with water (30 ml) and extracted with three 10 ml portions of chloroform. The combined chloroform extracts were washed

with water, dried, and evaporated to give 210 mg of a white solid, m.p. 124–214°. Recrystallization from xylene afforded 180 mg of fine white crystals, m.p. 241–242°. A mixture m.p. with meso-stilbene dibromide (30) was not depressed and the i.r. spectra of the two compounds were identical.

Oxidation of 1-Phenylpropyne

1-Phenylpropyne (512 mg, 4.41 mmol, freshly distilled) was dissolved in anhydrous DMSO (10 ml), the solution was stirred, and NBS (798 mg, 4.46 mmol) was added in one portion. A yellowish-orange color formed immediately and the reaction mixture became warm. The flask was fitted to a reflux condenser equipped with a calcium chloride drying tube and the contents were stirred at 90° for 45 h. By this time the solution was deep yellow. The solution was cooled, poured into 30 ml of a 1:1 mixture of petroleum ether (30–60°) and benzene, and water (10 ml) was added. When this mixture was shaken the yellow color diminished in intensity but the organic layer remained pale yellow. It was washed with nine 10 ml portions of water. The combined aqueous extracts were then back extracted with 20 ml of petroleum ether (30–60°) and the combined organic extracts, after drying over magnesium sulfate, were evaporated to give 993 mg of an orange oil. Integration of the methyl region of the n.m.r. spectrum of this oil and comparison with the spectra of standard mixtures revealed the oil to contain **12** (40%), **13** (22%), **14** (8%), and unreacted 1-phenylpropyne (14%). Based on acetylene consumed, the conversion to **12** is 47%.

The oil obtained from an oxidation conducted at room temperature with 2 mol equiv of NBS per mol of 1-phenylpropyne was heated under reflux for 0.5 h with *p*-nitrophenylhydrazine (0.5 g), ethanol (15 ml), and acetic acid (2 drops). The precipitated solid was collected by filtration and, after recrystallization from ethanol, melted at 254–255°. The reported m.p. of 1-phenylpropanedione di-*p*-nitrophenylhydrazone is 256–257° (31).

Oxidation of 2-Butyne

A solution of 2-butyne (0.2 ml) and NBS (712 mg, 4 mmol) in anhydrous DMSO (10 ml) was stirred at room temperature for 26 h. The yellow reaction mixture was then diluted with water (50 ml) and extracted with four 25 ml portions of ether. The yellow color remained in the organic layer. This layer was dried over magnesium sulfate and concentrated under reduced pressure at 20°. The residue was treated with water (10 ml) and 85% hydrazine hydrate (1 ml) and the resulting mixture stirred at room temperature for 2 h. The oil which separated during this period was extracted into chloroform. The chloroform extract was dried over anhydrous magnesium sulfate and evaporated. The semi-solid product was recrystallized from ethanol to give biacetyldihydrazone, m.p. 155–157° (lit. (32) 158°).

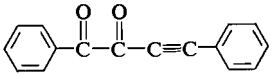
Oxidation of Phenylacetylene

A solution of phenylacetylene (306 mg, 3 mmol) and NBS (534 mg, 3 mmol) in anhydrous DMSO (10 ml) was stirred at room temperature for 20 h. The yellow mixture was then diluted with water (50 ml) and extracted with three 40 ml portions of ether. The ether extract was dried and evaporated. The i.r. spectrum of the resulting yellow oil showed a single strong carbonyl peak at 5.85 μ. The oil was treated with a solution of *p*-nitrophenylhydrazine (0.6 g) and glacial acetic acid (2 drops) in ethanol (15 ml). The resulting solution was refluxed for 0.5 h; during this period a deep red solid precipitated. This was collected and recrystallized from ethanol. It melted at 309–311° (phenylglyoxal di-*p*-nitrophenylhydrazone melts at 310–311.5° (33)).

In a second experiment, conducted with the same quantities of materials, the total reaction mixture was treated after 20 h with *p*-nitrophenylhydrazine (2.0 g), and stirring was continued for an additional 2.5 h. Addition of water precipitated a dark solid which was collected, washed with ethanol, and dried *in vacuo*. The di-*p*-nitrophenylhydrazone weighed 317 mg (corresponding to a 25% recovery, based on starting acetylene) and melted at 308–310°.

Oxidation of Diphenylbutadiyne

(*a*) Diphenylbutadiyne (116.3 mg, 0.58 mmol) was stirred in anhydrous DMSO (3 ml) at room temperature, and NBS (414 mg, 2.32 mmol, 4 mol equiv) was added in portions during a 10 min period. After 2 h the solution, now orange and strongly acidic, was diluted with water (10 ml) and extracted with methylene chloride. This extract was washed with water until the washings were neutral, and then dried over anhydrous magnesium sulfate and evaporated to dryness. The resulting yellow oil showed i.r. absorption at 3.0, 3.3, 4.56 (w), 5.8–6.05 (s), 6.3, 6.7, 6.9, 7.65, and 8.9 μ. The presence of both carbonyl and acetylenic stretching bands suggests that the initial stage of the reaction affords **23** rather than **24**. The t.l.c. analysis of the oil showed it to consist mainly of unreacted diphenylbutadiyne. Therefore, the yellow



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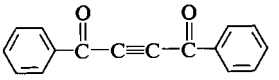

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oil was redissolved in DMSO (3 ml) and the solution treated with NBS (0.4 g, 2.3 mmol). After 48 h the now bright red solution was diluted with water and extracted with methylene chloride to give, after drying and evaporation of the solvent, a red oil. The t.l.c. analysis showed this oil to contain only a trace of diphenylbutadiyne; its i.r. spectrum showed broad carbonyl absorption at 5.8–6.0 μ. Attempts to crystallize the oil from a variety of solvents were unsuccessful. The oil turned yellow when placed on a column of alumina (Woelm, grade IV), but no material could be eluted.

(*b*) Diphenylbutadiyne (202 mg, 1.0 mmol) and NBS (356 mg, 2 mmol) were dissolved in anhydrous DMSO (10 ml) and the solution was stirred at room temperature for 3 days. The deep red solution was then evaporated to dryness under high vacuum. When the red residue was treated with water (0.4 ml) it immediately turned yellow. Sulfuric acid (0.6 ml) and nitric acid (0.3 ml) were then added and the mixture was refluxed for 1 h. Then glacial acetic acid (1 ml) was added and the mixture was re-

fluxed for a further 2 h (22). Addition of water (10 ml) followed by extraction with petroleum ether, drying of the organic extract and evaporation, afforded a yellow solid. After two recrystallizations from petroleum ether (30–60°) this yellow solid melted at 93–94°. A mixture m.p. with benzil was not depressed.

(*c*) The above experiment was repeated and, after evaporation of the DMSO and addition of water (red → yellow), the mixture was extracted with carbon tetrachloride. The yellow carbon tetrachloride extract was dried and concentrated; after the residue had been maintained at 0.1 mm for 0.5 h it turned red. When this residue was exposed to air the yellow color reappeared instantly. The residue was dissolved in benzene and the yellow solution subjected to slow distillation. After a part of the benzene (and the trace of water) had been removed, the red color reappeared,

(*d*) Diphenylbutadiyne (1.0 g, 5 mmol) was dissolved in anhydrous DMSO (10 ml), and NBS (1.80 g, 10 mmol) was added in four portions at 3 h intervals. When the addition was complete the solution was stirred for 30 h and then extracted with three 100 ml portions of petroleum ether (30–60°) to remove the traces of unreacted diphenylbutadiyne. The red DMSO phase was then diluted with water (50 ml) (red → yellow) and extracted with three 50 ml portions of ether. The ether extract was washed thoroughly with water, dried, and evaporated to a residue which weighed 1.5 g. This residue was dissolved in ethanol (20 ml), hydroxylamine hydrochloride (690 mg, 10 mmol) was added, and this solution was refluxed briefly and then allowed to stand overnight. Water was added, the mixture extracted with chloroform, and the dried chloroform extract evaporated. The resulting product was purified by column chromatography on silica gel (25 g) with graded mixtures of petroleum ether (30–60°) and ether. Recrystallization from benzene–petroleum ether gave the dioxime of diphenyltetraketone, m.p. 173–175° dec. (lit. (20) 176°).

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