Reactive Intermediates. Part II.[1] Some Addition Reactions of Benzyne

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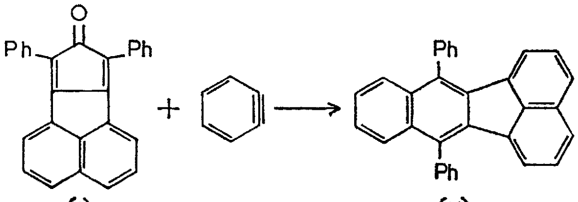
Benzyne, generated by the oxidation of 1-aminobenzotriazole with lead tetra-acetate, adds to 1,3-dienes and reacts with nucleophiles in moderate to excellent yields. However, it generally dimerises much faster than it adds to heterocyclic dienes. Addition of benzyne to 2-methyl- and 2-benzyl-benzotriazole gives 1-phenylbenzotriazole. Mechanisms for these reactions are proposed. Benzyne, generated oxidatively, does not add appreciably to mono-olefins.

THE preceding paper[1] describes the generation of benzyne under mild conditions by the oxidation of 1-aminobenzotriazole with lead tetra-acetate. In the absence of suitable trapping agents, biphenylene is formed in high yield, with small amounts of triphenylene and, under certain conditions, 2-acetoxybiphenylene. We now report the reactions of benzyne, generated by this oxidative route, with 1,3-dienes and other nucleophiles.

In general, a solution of 1-aminobenzotriazole (1 equivalent) in a dry solvent (or in the diene if liquid) was added to a stirred solution or suspension of lead tetra-acetate (1·2 equiv.) in the same solvent at 20° containing an excess of the other reactant. Gas evolution was instantaneous and ceased on completion of addition of amine. The products were isolated by column chromatography.

Thus, with tetraphenylcyclopentadienone (tetracyclone, 3 equiv.) the adduct, 1,2,3,4-tetraphenylnaphthalene (95%), was isolated. No biphenylene was detected when the reaction was carried out in benzene, but the benzyne dimer was produced (5%) in methylene chloride, together with the adduct (88%). Analogous oxidations of 5-methyl- and 7-methyl-1-aminobenzotriazole in the presence of tetracyclone gave 6-methyl-1,2,3,4-tetraphenylnaphthalene (99%) and 5-methyl-1,2,3,4-tetraphenylnaphthalene (83%) respectively. Similarly, 2,5-di-*p*-anisyl-3,4-diphenylcyclopentadienone gave 1,4-di-*p*-anisyl-2,3-diphenylnaphthalene (80%). In all these reactions, the excess of dienone was recovered quantitatively. The structures of the adducts followed from their analytical and spectral properties. The addition of benzyne to the related dienone, 7,9-diphenyl-8*H*-cyclopent[*a*]acenaphthylen-8-one [acecyclone, (I)] gave the fluorescent adduct, 7,12-diphenylbenzo[*k*]fluoranthene (II) in only 8% yield, with a 50% yield of biphenylene. The low yield of adduct in this reaction was due to the insolubility of the dienone; indeed, the oxidation had to be carried out in refluxing ethyl acetate to effect any reaction at all, apart from the dimerisation of benzyne. The structure of the adduct (II) was confirmed by its synthesis from the Diels–Alder adduct of 1,3-diphenylisobenzofuran with acenaphthylene.[2]

Oxidation of 1-aminobenzotriazole with lead tetra-acetate in furan gave, on distillation, 1,4-epoxy-1,4-dihydronaphthalene (80%), which underwent acid-catalysed isomerisation to 1-naphthol, as reported.[3] The formation of the benzyne adduct from 1,3-diphenylisobenzofuran was complicated by competing oxidation of the diene to *o*-dibenzoylbenzene, but with a large excess of the diene, 9,10-oxido-9,10-diphenyldihydroanthracene was obtained in reasonable yield (43%). The adduct was reduced to 9,10-diphenylanthracene in high yield, as reported.[4]



(I) (II)

Generation of benzyne in the presence of 3 equivalents of anthracene resulted in a high yield of biphenylene; the adduct, triptycene, was isolated in low yield (12%), together with a trace of anthraquinone, a known product of oxidation of anthracene with lead tetra-acetate.[5] No evidence for the addition of benzyne to the A-ring of anthracene was found.[6]

Oxidation of 1-aminobenzotriazole with lead tetra-acetate in cyclohexa-1,3-diene gave a two-component hydrocarbon fraction from chromatography. One of these was biphenyl (25%), presumably formed by the oxidation of 5-phenylcyclohexa-1,3-diene and 3-phenylcyclohexa-1,4-diene, the phenylation products observed by Huisgen[7] in this reaction, using different sources of benzyne. The other component of the hydrocarbon mixture was shown to be the 1,4-adduct, benzobicyclo[2,2,2]octadiene (61%), by spectral data and by its hydrogenation to the crystalline benzobicyclo[2,2,2]octene and its pyrolysis to naphthalene.[8]

Addition of benzyne to the 1,3-dipole, phenyl azide, gave the expected adduct, 1-phenylbenzotriazole (45%). No other products could be isolated in this reaction. With thionylaniline, a complex mixture of highly coloured amorphous products was obtained, from which a small amount of 6*H*-dibenzo[*c*,*e*][1,2]thiazine 5,5-dioxide (III) was isolated. This compound was charac-

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[1] Part I, C. D. Campbell and C. W. Rees, preceding paper.

[2] E. Bergmann, *J. Amer. Chem. Soc.*, 1952, **74**, 1075.

[3] G. Wittig and L. Pohmer, *Angew. Chem.*, 1955, **67**, 348.

[4] G. Wittig, E. Knauss, and K. Niethammer, *Annalen*, 1960, **630**, 10.

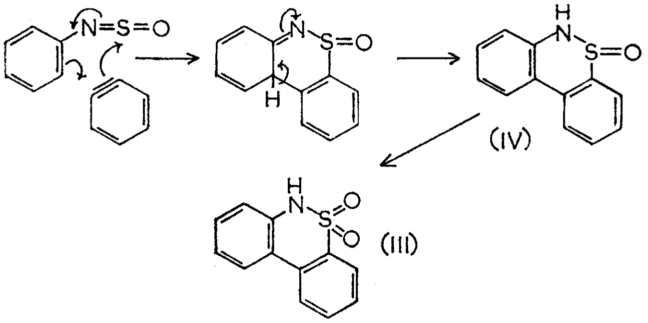
[5] L. F. Fieser and S. T. Putnam, *J. Amer. Chem. Soc.*, 1947, **69**, 1038.

[6] B. H. Klanderman, *J. Amer. Chem. Soc.*, 1965, **87**, 4649.

[7] R. Huisgen and R. Knorr, *Tetrahedron Letters*, 1963, 1017.

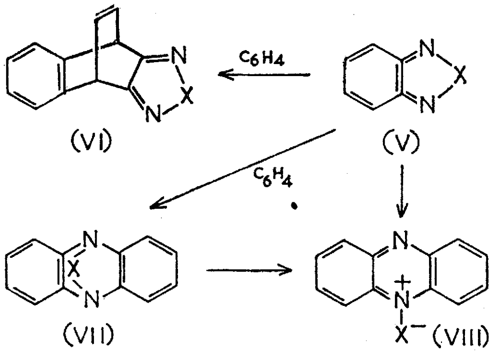
[8] K. Kitahonoki and Y. Takano, *Tetrahedron Letters*, 1963, 1597; K. Tori, Y. Takano, and K. Kitahonoki, *Chem. Ber.*, 1964, **97**, 2798.

terised by its i.r. and mass spectra and by comparison with an authentic sample. Its mode of formation is presumably similar to that of phenanthridone from the reaction of benzyne with phenyl isocyanate,[9] involving 1,4-addition of benzyne to the substrate, followed by aromatisation to the sulphinamide (IV) which, under the oxidative conditions employed, is converted into the sulphonamide (III).



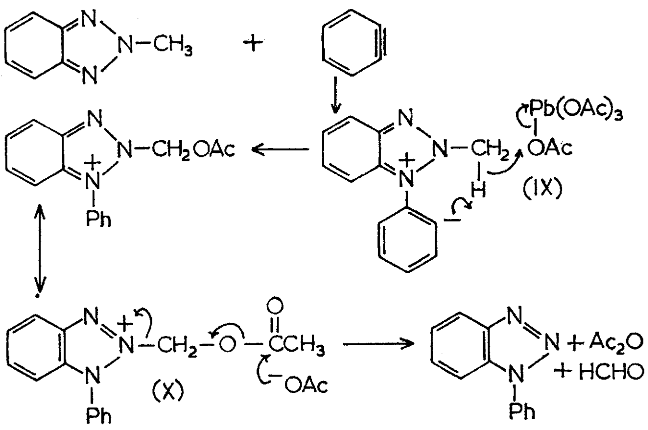
In the presence of a large excess of benzoic acid, the oxidation of 1-aminobenzotriazole with lead tetra-acetate gave biphenylene and phenyl benzoate in approximately equal amounts. However, when the oxidation was performed in ethanol, phenetole was the sole product obtained in about 60% yield. Somewhat surprisingly, benzyne added to bromine much faster than it dimerised, *o*-dibromobenzene being the only product obtained (75%) when the reaction was carried out in the presence of 1 mol. of bromine. Benzyne generated by other methods has been shown to add halogens.[10]

The preceding reactions of benzyne, generated oxidatively, show that it readily adds to dienes and nucleophiles to give adducts in low to virtually quantitative yields. We next hoped to extend these additions to diene systems containing 'terminal' nitrogen atoms. Thus, 1,4-addition of benzyne across the 'heterodiene' system in (V; X = O, S, Se, NR) would give the bridged phenazine (VII), which, depending on the nature of the heteroatom X, could rearrange to compound (VIII), for example, phenazine *N*-oxide (X = O), or could extrude X to give phenazine with, for example, X = S or Se. Alternatively, addition of benzyne across the quinonoid diene system would give compounds of type (VI).



However, it was found that when 1-aminobenzotriazole was oxidised with lead tetra-acetate in the presence of an excess of compounds of type (V), the benzyne dimer, biphenylene, was often the only isolable compound. Thus, using benzofurazan (V; X = O) or benzofuroxan (V; X = O, *N*-oxide), no adducts were detected and biphenylene was isolated in 86% and 48% yield respectively. In the presence of the monocyclic diene, 3,4-dimethylfurazan, no quinoxaline derivative was detected even when the furazan was used as solvent; biphenylene (32%) was isolated. The addition of benzyne to 2,1,3-benzothiadiazole (V; X = S) again gave biphenylene (59%), but also afforded a 10% yield of two isomeric 1 : 1 adducts. Analogous adducts were obtained in 92% yield by the addition of benzyne to 2,1,3-benzoselenadiazole (V; X = Se). The structures of these compounds will be reported in a future communication.

The oxidation of 1-aminobenzotriazole in 2-methylbenzotriazole (V; X = NMe) gave 1-phenylbenzotriazole (22%). No biphenylene was detected. One possible mechanism for the formation of this compound is initial quaternisation by benzyne on N(1) to give the betaine (IX) followed by intramolecular hydrogen abstraction from the methyl group and attack by lead tetra-acetate to give the acetate (X). This species then fragments to the product by attack of acetate, with the formation of acetic anhydride and formaldehyde, the latter probably being oxidised to formic acid under these conditions. Support for this mechanism was obtained when the reaction was carried out in 2-benzylbenzotriazole (V; X = $N{\cdot}CH_2Ph$). 1-Phenylbenzotriazole was obtained, as expected, together with a small amount of benzoic acid, which was not detected in the reaction of 2-benzylbenzotriazole with lead tetra-acetate. 1-Phenylbenzotriazole was not obtained when the reaction was carried out in the presence of a large excess of 2-benzylidenaminobenzotriazole (V; X = N·N=CHPh). Biphenylene was the sole product obtained in this reaction.



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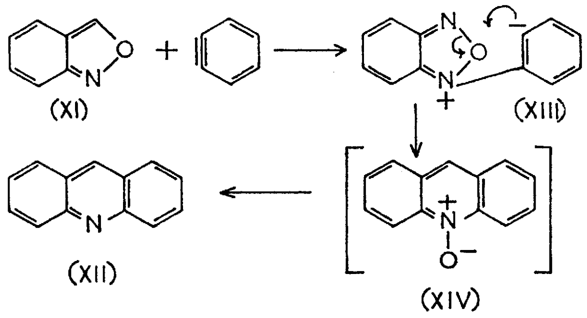
Oxidation of 1-aminobenzotriazole in the presence of 1-methylbenzotriazole gave biphenylene only. It was expected that this reaction might give 2-phenylbenzotriazole by a similar route to that proposed above, with initial quaternisation by benzyne on N(2).

The reluctance of benzyne to add 1,4 across these terminal nitrogen dienes prompted an investigation of anthranil (XI), a diene with only one hetero-terminal atom. Oxidation of 1-aminobenzotriazole in the presence of an excess of anthranil afforded not only biphenylene (7%) but also acridine (XII) (5%). However, the acridine was probably formed by initial quaternisation of nitrogen by benzyne to give the betaine (XIII), rather than by a concerted Diels–Alder addition. The *N*-oxide (XIV) is probably formed and deoxygenated under the reaction conditions, in accord with the well established facile deoxygenation of *N*-oxides of weakly basic amines.[11] Attempted addition of benzyne to acridine itself, in the hope of producing the interesting 9-azatriptycene, met with no success, biphenylene being the only recognisable product isolated. Similarly, biphenylene was the only identifiable compound isolated from the reaction of benzyne with phenazine, although a complex mixture of highly coloured products was obtained, possibly arising from phenazyl radicals.



Unlike 1,8-dehydronaphthalene, generated by oxidation of 1-aminonaphtho[1,8-*d*,*e*]triazine with lead tetra-acetate, which adds to olefins stereospecifically,[12] benzyne generated in this manner in the presence of mono-enes dimerises. Thus, when the oxidation of 1-aminobenzotriazole was carried out in both *cis*- and *trans*-dichloroethylene, biphenylene was obtained in reasonable yield. Surprisingly, 2-acetoxybiphenylene was formed in considerably greater yield (8%) than normal, in both cases. Benzyne generated from benzenediazonium-2-carboxylate has been shown to add to vinyl acetate in good yield.[13] However, oxidative generation of benzyne in vinyl acetate gave biphenylene in high yield and only trace amounts of the 1,2-adduct, benzocyclobutenyl acetate, and 2-acetoxybiphenylene. Similarly, biphenylene was the only compound isolated from attempted additions to tetracyanoethylene and tetracyanoethylene oxide.

EXPERIMENTAL

General Procedure.—1-Aminobenzotriazole (3 mmoles) was dissolved in a dry solvent (*ca.* 20 ml.) and added dropwise during 3 min. to a magnetically stirred solution (or suspension) of lead tetra-acetate (3·5 mmoles) and the diene or nucleophile in the same dry solvent (*ca.* 20 ml.) at 20°. After stirring for 5 min., the lead diacetate was filtered off and the filtrate evaporated on to, and eluted from, a suitable adsorbent for column chromatography. Products were eluted with petroleum (b.p. 40—60°), petroleum–ether, ether, and ether–methanol, with gradual variation of the solvent composition.

The individual oxidations are described as follows.

Diene or Nucleophile.—Amount of diene or nucleophile used, solvent, temperature of reaction if other than 20°, adduct(s), (yield of adduct), properties of the adduct(s). Additional experimental data are included at the end of each section.

Tetracyclone.—(*a*) 6 mmoles, benzene, 1,2,3,4-tetraphenylnaphthalene, (95%), m.p. 204—206° (from benzene–ethanol) (lit.,[14] 204°). The excess of tetracyclone was recovered quantitatively.

(*b*) 6 mmoles, methylene chloride, biphenylene (5%), m.p. 110—111° (from ethanol) (lit.,[15] 110°); 1,2,3,4-tetraphenylnaphthalene (88%).

(*c*) From 1-amino-5-methylbenzotriazole (3 mmoles) and tetracyclone (6 mmoles) in benzene was obtained 6-*methyl*-1,2,3,4-*tetraphenylnaphthylene* (99%), m.p. 221—223° (from benzene–ethanol) (Found: C, 93·8; H, 5·8. $C_{35}H_{26}$ requires C, 94·1; H, 5·9%), $\lambda_{max.}$ 223 (log ε 4·77), 245 (4·86), 295 mμ (4·14). The excess of tetracyclone was recovered quantitatively.

(*d*) From 1-amino-7-methylbenzotriazole (3 mmoles) and tetracyclone (9 mmoles) in methylene chloride was obtained 5-*methyl*-1,2,3,4-*tetraphenylnaphthalene* (83%), m.p. 242—243° (from benzene–ethanol) (Found: C, 94·2; H, 6·0%), $\lambda_{max.}$ 225 (log ε 4·76), 244 (4·81), 301 mμ (4·21). The excess of tetracyclone (100%) was recovered.

2,5-*Di*-p-*anisyl*-3,4-*diphenylcyclopentadienone.*[16]— 6 mmoles, benzene, 1,4-di-*p*-anisyl-2,3-diphenylnaphthalene (80%), m.p. 219—220° (from benzene–ethanol) (lit.,[17] 221·5—222°) (Found: C, 87·4; H, 5·8. Calc. for $C_{36}H_{28}O_2$: C, 87·8; H, 5·7%). The excess of dienone (100%) was recovered,

Acecyclone.[18]—6 mmoles, ethyl acetate, 76°, biphenylene (50%), 7,12-diphenylbenzo[*k*]fluoranthene (8%), m.p. 276—277° (from n-butanol) (lit.,[2] 267°), mixed m.p. 278° (Found: C, 94·9; H, 5·0. Calc. for $C_{32}H_{20}$: C, 95·0; H, 5·0%). An authentic specimen was prepared by the method of Bergmann,[2] m.p. 277—278°.

Furan.—Furan was used as the solvent, and the adduct was distilled from the reaction mixture to give 1,4-epoxy-1,4-dihydronaphthalene, (80%), b.p. *ca.* 80°/0·5 mm., m.p. 50—51° [from petroleum (b.p. 60—80°)] (lit.,[3] 55—56°). The adduct was converted into 1-naphthol (90%), m.p. 93°,

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[13] H. H. Wasserman and J. Solodar, *J. Amer. Chem. Soc.*, 1965, **87**, 4002.

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[18] W. Dilthey, I. ter Horst, and W. Schommer, *J. prakt. Chem.*, 1935, **143**, 189.

by treatment with refluxing methanolic hydrogen chloride solution.

1,3-*Diphenylisobenzofuran*.—10 mmoles, benzene, 9,10-oxido-9,10-diphenyldihydroanthracene (43%), m.p. 193° [from benzene–petroleum, b.p. 60—80°)] (lit.,[4] 188°). The adduct was converted into 9,10-diphenylanthracene (100%), m.p. 249—251° (from acetic acid) (lit.,[4] 245—247°), by treatment with zinc dust in refluxing glacial acetic acid. In this oxidation, sufficient lead tetra-acetate was added at the end of the reaction to convert the excess of 1,3-diphenylisobenzofuran into *o*-dibenzoylbenzene, m.p. 148—149° (from aqueous acetone).

Anthracene.—9 mmoles, benzene 80°, biphenylene (59%), triptycene (12%), m.p. 249—250° (from ethanol) (lit.,[6] 253—254°), 9,10-anthraquinone (1%), m.p. 281°. The excess of anthracene was removed by converting it into the maleic anhydride adduct.

Cyclohexa-1,3-*diene*.—The diene was used as the solvent. G.l.c. (10% Apiezon L on 60—72 Celite at 200°) of the hydrocarbon fraction from column chromatography showed benzobicyclo[2,2,2]octa-2,5-diene (*ca.* 60%) and biphenyl (*ca.* 25%). A portion of the mixture was hydrogenated (10% Pd–C) in ethanol and the products were chromatographed to give benzobicyclo[2,2,2]octene, m.p. 60° (lit.,[8] 61—62°), and biphenyl, m.p. 70°. A further portion of the hydrocarbon mixture was heated at 300° for 2 hr.; naphthalene, m.p. 80°, and biphenyl, m.p. 70°, sublimed.

Phenyl Azide.—The azide was used as solvent. The excess of phenyl azide was removed by steam-distillation. Extraction of the residue with ether and chromatography gave 1-phenylbenzotriazole (45%), m.p. 87—88° [from ether–petroleum (b.p. 40—60°)] (lit.,[19] 89—90°) (Found: C, 74·0; H, 4·6; N, 21·4. Calc. for $C_{12}H_9N_3$: C, 73·9; H, 4·6; N, 21·5%).

Thionylaniline.[20]—The trap was used as solvent. The excess of thionylaniline was removed by distillation *in vacuo*, and the residue chromatographed to give 6*H*-dibenzo[*c,e*][1,2]thiazine 5,5-dioxide (4%), m.p. 193° after sublimation (lit.,[21] 196°), $\nu_{max.}$ 3160 (NH), 1300, 1150 (SO_2), 750 cm.$^{-1}$ (i.r. identical with that of an authentic sample). A complex mixture of highly coloured amorphous solids was also obtained but not investigated.

Benzoic Acid.—30 mmoles, benzene, biphenylene (20%), phenyl benzoate (20%), m.p. 67—68°. The excess of benzoic acid was removed with dilute aqueous alkali before chromatography.

Ethanol.—Ethanol was used as the solvent. Phenetole (*ca.* 60%) was isolated by chromatography and identified by comparison of its i.r. spectrum with that of an authentic sample.

Bromine.—3 mmoles, methylene chloride, *o*-dibromobenzene (*ca.* 75%), identified by i.r. comparison, and nitration to give 1,2-dibromo-4-nitrobenzene, m.p. and mixed m.p. 55° (lit.,[22] 58—59°).

Benzofurazan.—6 mmoles, benzene, 10°, biphenylene (86%). The excess of benzofurazan was recovered (69%).

Benzofuroxan.—6 mmoles, benzene, 25°, biphenylene (48%). The excess of benzofuroxan was recovered (91%).

3,4-*Dimethylfurazan*.—The diene was used as the solvent. The excess of the furazan was removed by distillation and the residue chromatographed to give biphenylene (32%) only.

2-*Methylbenzotriazole*.[23]—The diene was used as the solvent. The excess of the diene was removed by distillation *in vacuo*, and the residue chromatographed to give 1-phenylbenzotriazole (22%), m.p. and mixed m.p. 87—88°, after sublimation.

2-*Benzylbenzotriazole*.[24]—The diene was used as the solvent at 35°. The reaction mixture was diluted with ether after the oxidation, filtered, and extracted with dilute aqueous alkali. The aqueous extract was acidified to give benzoic acid (*ca.* 2%), m.p. 121°. The ethereal solution was extracted with 24% aqueous hydrochloric acid to remove most of the 2-benzylbenzotriazole (no 1-phenylbenzotriazole was detected in the acid extract). From the ethereal solution, on chromatography, was obtined 1-phenylbenzotriazole (12%), m.p. and mixed m.p. 87—88°. A similar reaction omitting 1-aminobenzotriazole gave no benzoic acid.

1-*Methylbenzotriazole*.[23]—9 mmoles, benzene, biphenylene (43%), 2-acetoxybiphenylene (1%), m.p. 89°, identified by i.r. comparison.

2-*Benzylidenaminobenzotriazole*.[1]—6 mmoles, methylene chloride, biphenylene (52%). The anil was recovered (96%).

Anthranil.—1-Aminobenzotriazole (3 mmoles) was dissolved in anthranil (32 mmoles) and added to lead tetra-acetate (3·5 mmoles) under benzene. On completion, the reaction mixture was steam-distilled to remove anthranil and the residue chromatographed to give acridine (5%), m.p. and mixed m.p. 110° after sublimation.

Acridine.—7·5 mmoles, benzene, 50°, biphenylene (21%), small amount of unknown compound, m.p. 270—271° (from ethanol) (Found: C, 80·6; H, 5·1; N, 7·9%). Acridine (69%) was recovered.

Phenazine.—7·5 mmoles, benzene, biphenylene (14%) and a complex mixture of red, blue, and purple crystals. Phenazine (72%) was recovered.

cis-*Dichlorethylene*.—The olefin was used as the solvent; biphenylene (38%), 2-acetoxybiphenylene (8%), m.p. 88—89°, after sublimation.

trans-*Dichlorethylene*.—The olefin was used as the solvent; biphenylene (58%), 2-acetoxybiphenylene (8%), m.p. 89—90°.

Vinyl Acetate.—The olefin was used as the solvent at −78°; biphenylene (77%), benzocyclobutenyl acetate (trace), and 2-acetoxybiphenylene (trace). The last two compounds were obtained as a mixture, the i.r. spectrum of which contained all the peaks of the individual spectra of benzocyclobutenyl acetate (prepared by the method of Wasserman and Solodar [13]) and 2-acetoxybiphenylene.

Tetracyanoethylene.—9 mmoles, benzene, biphenylene (68%), black polymers.

Tetracyanoethylene Oxide.—9 mmoles, benzene, 80°, biphenylene (7%), intractable tars.

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