Molecular weights were determined by thermoelectric measurement.

Reduction of Bispirodienone 6 (Standard Procedure).—A solution of bispirodienone 6 (R = H)[2] (575 mg, 1 mmol) and benzpinacol (400 mg, 1.09 mmol) in dimethylformamide (6 ml) was kept at 160° for 3 min. Addition of water to the colorless solution gave a crystalline precipitate of bisphenol 5 (R = H): yield 560 mg (97%); mp 233–234°. The mixture melting point with authentic[2] material was not depressed.

3,5-Di-*t*-butyl-4′-phenylfuchsone (4, R = Phenyl).—A solution of 4-phenylbenzophenone (1, R = phenyl) (1.29 g, 5 mmol) and 2,6-di-*t*-butylphenol (2.06 g, 10 mmol) in acetone (60 ml) was irradiated (GE 100-W AH/4) under nitrogen for 4 hr. Vacuum evaporation of solvent from the light yellow reaction mixture gave an oily residue from which 100 mg (7.7%) of 4-phenylbenzophenonepinacol, mp 193–195°, was removed by filtration after treatment with 10 ml of methanol. Upon acidification of the methanol filtrate with 1 drop of concentrated hydrochloric acid dissolved in 1 ml of methanol, the yellow-orange 3,5-di-*t*-butyl-4′-phenylfuchsone precipitated. It was removed by filtration and recrystallized from a boiling chloroform–methanol mixture: yield 1.42 g (63%); mp 192–193°; uv spectrum (in CH_3OH) λ_{max} 283 mμ (ϵ 19,000), 387 (31,500).

Anal. Calcd for $C_{33}H_{34}O$: C, 88.74; H, 7.67; mol wt, 446.64. Found: C, 88.80; H, 7.77; mol wt (in benzene), 438.

4,4′-Dihydroxy-4″-phenyl-3,3′,5,5′-tetra-*t*-butyltetraphenylmethane (5, R = Phenyl).—A suspension of 4-phenylbenzophenone (1.29 g, 5 mmol) in a solution of 2,6-di-*t*-butylphenol (1.54 g, 7.5 mmol) in methanol (65 ml) containing hydrochloric acid (0.1 ml) was irradiated under nitrogen for 3 hr (Philips HPK, 125 W). A colorless precipitate formed as the benzophenone dissolved during the reaction. Partial vacuum evaporation of the solvent gave 1.7 g of crystalline residue. It was treated with 200 ml of boiling methanol. Hot filtration gave 200 mg (15%) of methanol-insoluble 4-phenylbenzophenonepinacol, mp 198–199° (lit.[8] mp 198–199°).

Anal. Calcd for $C_{38}H_{30}O_2$: C, 88.00; H, 5.83; mol wt, 518.62. Found: C, 87.85; H, 5.82.

After partial vacuum evaporation of the solvent from the filtrate crystalline bisphenol 5 (R = phenyl) precipitated: yield 1.3 g (53%); mp 169–170°.

Anal. Calcd for $C_{47}H_{56}O_2$: C, 86.45; H, 8.65; mol wt, 652.92. Found: C, 86.31; H, 8.82; mol wt (in acetone), 610.

Oxidation of 4,4′-Dihydroxy-4″-phenyl-3,3′,5,5′-tetra-*t*-butyltetraphenylmethane (6, R = Phenyl).—A suspension of active manganese dioxide[9] (6.5 g) in a solution of 5 (R = phenyl) (652 mg, 1 mmol) in benzene (50 ml) was shaken for 30 min. Filtration and vacuum evaporation of the filtrate gave a solid orange residue which was recrystallized by dissolving it in a little warm benzene and adding methanol: yield 600 mg (92%); mp 240–250° dec; ir spectrum (in KBr), no OH absorption, cyclohexadienone absorption at 1620–1645 cm^{-1}.

Anal. Calcd for $C_{47}H_{54}O_2$: C, 86.72; H, 8.36; mol wt, 650.90. Found: C, 86.56; H, 8.36; mol wt (in benzene), 639.

Registry No.—4 (R = Ph), 19886-68-1; 5 (R = Ph), 19886-69-2; 6 (R = Ph), 19922-48-6.

[8] M. Gomberg and W. E. Bachmann, *J. Amer. Chem. Soc.*, **49**, 236 (1927).

[9] J. Attenburrow, A. F. B. Cameron, J. H. Chapman, R. N. Evans, B. A. Hems, A. B. A. Jansen, and T. Walker, *J. Chem. Soc.*, 1094 (1952).

The Action of Triethyl Phosphite on 1,5-Diphenyl-3-methyl-4-nitrosopyrazole. A Novel Cleavage of the Pyrazole Ring

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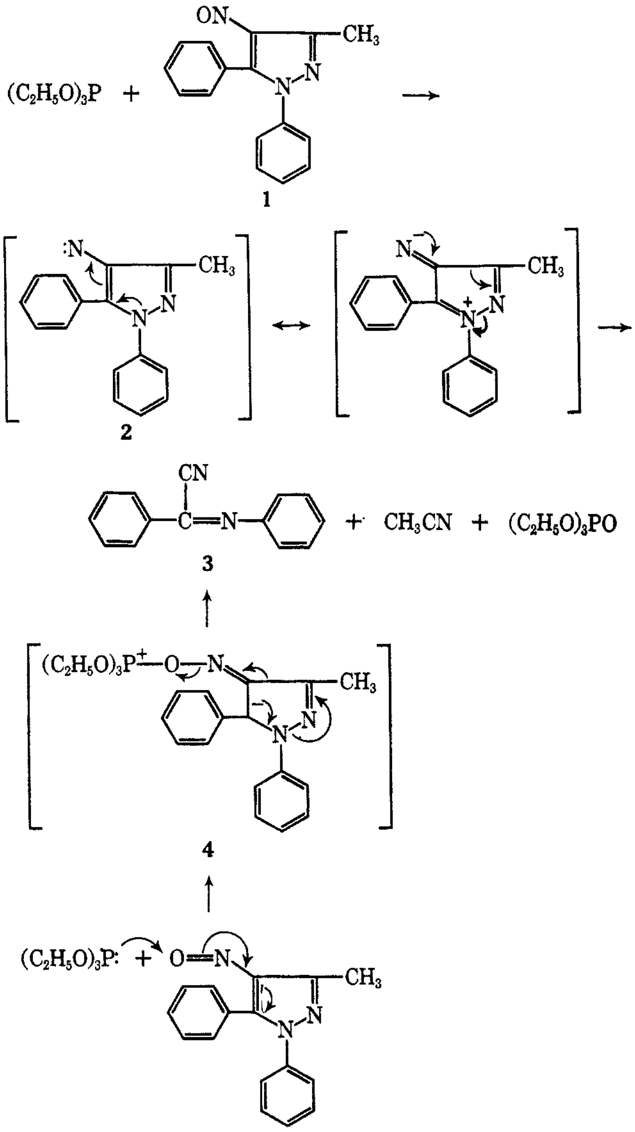
Bunyan and Cadogan[1,2] have shown that 2-nitrosodiphenyl reacts with triethyl phosphite at 0–5° in benzene solution to give carbazole in 78% yield. It was postulated that an intermediate nitrene may be involved.[2,3] We were interested in investigating the readily available 1,5-diphenyl-3-methyl-4-nitrosopyrazole[4] (1) in this reaction. The nitrene intermediate from 1 might lead to an indolo[2,3-*d*]pyrazole, but alternatively, the singlet nitrene might be expected also to attract electrons from the pyrazole ring.

SCHEME I



When 1,5-diphenyl-3-methyl-4-nitrosopyrazole (1) was treated with triethyl phosphite in benzene solution at 0–5°, according to the general method of Bunyan and Cadogan,[2] no apparent reaction took place. However, when the mixture was heated under reflux, a yellow solid, $C_{14}H_{10}N_2$, was isolated. The ir spectrum

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[1] P. J. Bunyan and J. I. G. Cadogan, *Proc. Chem. Soc.*, 78 (1962).

[2] P. J. Bunyan and J. I. G. Cadogan, *J. Chem. Soc.*, 42 (1963).

[3] J. I. G. Cadogan, *Quart. Rev.* (London), **22**, 222 (1968).

[4] C. N. O'Callaghan and D. Twomey, *Proc. Roy. Irish Acad. Sect. B.*, **64** (13), 187 (1965); *Chem. Abstr.*, **65**, 12191*d* (1966).

showed weak absorption at 2210 cm^{-1}, attributable to a nitrile group, and no NH or OH absorption. The nmr spectrum showed only aromatic protons and *no* CH_3 protons. These data were consistent with phenyl(phenylimino)acetonitrile (**3**), and this structure was confirmed by comparison (infrared, melting point, and nuclear magnetic resonance) with an authentic sample.[5]

Subsequently, it was found that the reaction could be carried out somewhat more conveniently by simply heating equimolar amounts of 1,5-diphenyl-3-methyl-4-nitrosopyrazole (**1**) and triethyl phosphite on the steam bath. An exothermic reaction took place and a small amount of liquid distilled from the reaction mixture. Redistillation of the distillate gave a colorless liquid boiling at 80° which was identified as acetonitrile. Phenyl(phenylimino)acetonitrile (**3**) was obtained from the reaction mixture in 70% yield.

The products obtained may be explained by the mechanism outlined in Scheme I. The reaction is thus a type of heterolytic fragmentation[6] which differs from those investigated previously in that a nitrene **2** may be involved as an intermediate. However, it is possible that a concerted reaction (*e.g.*, **4**) takes place without the formation of an intermediate nitrene.[7]

Experimental Section[8]

Phenyl(phenylimino)acetonitrile (5).—A mixture of 7.89 g (0.03 mol) of 1,5-diphenyl-3-methyl-4-nitrosopyrazole,[4] 4.98 g (0.03 mol) of triethyl phosphite, and 120 ml of dry benzene was heated under reflux for 13 hr using a condenser closed off with a calcium chloride tube. The benzene was removed by distillation and the residue was heated on the steam bath under vacuum (<1 mm). The oil was allowed to cool and was poured into water. The solid was removed by filtration and was recrystallized from ethanol. There was obtained 3.05 g of yellow prisms melting at 73–74°.

Anal. Calcd for $C_{14}H_{10}N_2$: C, 81.53; H, 4.89; N, 13.58. Found: C, 81.40; H, 4.82; N, 13.70; *m/e*, 206.

When equimolar amounts [7.89 g (0.03 mol) of 1,5-diphenyl-3-methyl-4-nitrosopyrazole and 4.98 g (0.03 mol) of triethyl phosphite] of reactants were heated on the steam bath without any solvent in a flask containing a side arm for distillation, an exothermic reaction took place and several milliliters of distillate was obtained. The residue was poured into water and the solid was removed by filtration and recrystallized from ethanol. There was obtained 4.34 g (70%) of yellow-green platelets melting at 67–71°. Further recrystallization from ethanol raised the melting point to 73–74°. The product was identical (mixture melting point and comparison infrared spectra) with that obtained above.

Registry No.—**1**, 7171-64-4; **3**, 4686-14-0; triethyl phosphite, 122-52-1.

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[5] F. Kröhnke, *Ber.*, **71B**, 2583 (1938). The reported melting point is 72°.

[6] *Cf.* C. A. Grob and P. W. Schiess, *Angew. Chem. Intern. Ed. Engl.*, **6**, 1 (1967).

[7] W. D. Crow and C. Wentrup [*Chem. Commun.*, 1082 (1968)] have recently investigated heterocyclic nitrenes in the pyridine and pyrimidine series and found that in these cases ring contraction takes place. The nitrenes were prepared by pyrolysis of triazolo[4,5-*b*]pyridine, tetraazolo-[1,5-*a*]pyrimidines, and related substances.

[8] All melting points and boiling points are corrected.

Formation of Thiols from Thiophene and Benzyne at 690°

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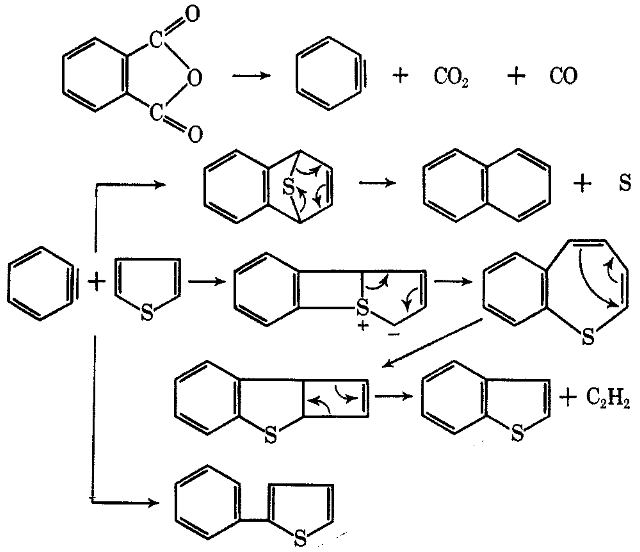
Benzyne from phthalic anhydride reacts with thiophene at 690° to give naphthalene and benzothiophene by 1,4 and 1,2 addition, respectively, as well as phenylthiophene by insertion (Scheme I).[1] The ratio of naphthalene to benzothiophene is about 9:1, implying nearly the same preference for 1,4 over 1,2 addition as was inferred from the reaction of benzyne with dichlorobenzenes and pyridine at the same temperature,[2,3] and reflecting the strong tendency of benzyne to act as a dienophile at high temperatures as well as in solution.[4]

SCHEME I



As the formation of naphthalene from phthalic anhydride and thiophene requires the extrusion of a sulfur atom, products arising from the reaction of such sulfur, possibly monatomic and hence highly reactive,[5] with thiophene might be expected. Sulfur atoms have been formed by photolysis of COS rather than by heating sulfur; the high S–S bond energy of about 101 kcal/mol[6] would ordinarily require temperatures at which

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[1] (a) E. K. Fields and S. Meyerson, *Chem. Commun.*, 708 (1966); (b) E. K. Fields and S. Meyerson in "Organosulfur Chemistry," M. J. Janssen, Ed., John Wiley & Sons, Inc., New York, N. Y., 1967, p 143.

[2] S. Meyerson and E. K. Fields, *Chem. Ind.* (London), 1230 (1966).

[3] E. K. Fields and S. Meyerson, *J. Org. Chem.*, **31**, 3307 (1966).

[4] G. Wittig, *Angew. Chem.*, **69**, 245 (1957); T. G. Corbett and O. N. Porter, *Aust. J. Chem.*, **18**, 781 (1965); W. L. Dilling, *Tetrahedron Lett.*, 939 (1966).

[5] K. S. Sidhu, E. M. Lown, O. P. Strausz, and H. E. Gunning, *J. Amer. Chem. Soc.*, **88**, 254 (1966).

[6] R. F. Palmer and F. P. Lossing, *ibid.*, **84**, 4661 (1962); J. Berkowitz and J. R. Marquart, *J. Chem. Phys.*, **39**, 275 (1963); H. Mackle, Abstracts of the Sulfur Symposium, Calgary, March 1964.