gen chloride was added to a pH 3–4 and the solution seeded with IIIc hydrochloride. On cooling to −15°, 0.19 g. (17%), of pure **IIIc hydrochloride** separated.

The filtrate, made basic with dilute, aqueous ammonia, yielded 0.54 g. (57%) of pure IIc.

F. **Aluminum Bromide and Ie.**—Cyclization of 1.0 g. of Ie hydrochloride was carried out as described for Ic. The residue from evaporation of the butanol–benzene extracts gave from 7 ml. of acetone (−5°), 0.22 g. of IIe, m.p. 240–246°.[12] The filtrate, concentrated to 2–3 ml., seeded with IIIe, and kept for 24–48 hr. at −15°, gave 0.35 g. of nearly pure IIIe; m.p. 198–205°; λ_{max}^{Nujol} 6.20 (s) μ.

Confirmation of IIa and IIIa Stereochemistry.[5]—Chloroform (20 ml.), 21.0 mg. of IIa, and 0.04 ml. of methyl iodide were left at 25° for 4 hr., and titrated with 0.0204 *N* acetous perchloric acid (Oracet Blue B indicator), 1.6 ml. being required. This corresponds to 33% of starting II or 67% methiodide formation in 4 hr. Similar reaction of 20.1 mg. of IIIa with 0.04 ml. of methyl iodide gave only 6.5% methiodide formation. These results are in accord with those observed for IIc and IIIc and leave no doubt that the orientation of the 9-methyl substituent in IIa and IIIa is as shown.[5]

A Simplified Procedure for the Preparation of Diazocyclopentadiene and Some Related Compounds

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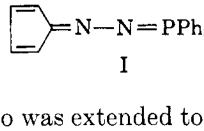
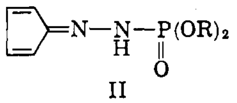
Diazocyclopentadiene previously has been prepared by Doering and DePuy[2] from *p*-toluenesulfonyl azide, cyclopentadiene, and phenyllithium. We have found in the present study that in this reaction phenyllithium can be replaced by almost any base, preferably by diethylamine or ethanolamine. The mixture of the reactants, cyclopentadiene, *p*-toluenesulfonyl azide, and the base, was simply left for some time at 0° and, after addition of water, was extracted with pentane. In view of its explosiveness[3] it seemed preferable not to isolate the diazocyclopentadiene in pure form but to use the pentane extracts directly for further reactions. These solutions were indeed sufficiently pure for most purposes. The diazocyclopentadiene formed was identified, and its yield determined by the isolation of (cyclopentadienylhydrazono)triphenylphosphorane[3] (I), the reaction product with triphenylphosphine.



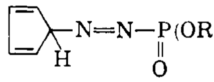
I

The reaction also was extended to diazoindene, which was prepared from indene, diethylamine, and *p*-toluenesulfonyl azide. In this case too, in order to avoid the isolation of the diazo compound itself, we prepared its derivative with triphenylphosphine. Diazofluorene, however, could not be prepared by this method. Both diazofluorene[4] and (fluorenylhydrazono)triphenylphosphorane[5] have been prepared earlier.

Furthermore we found that the reaction of diazocyclopentadiene with dialkyl phosphites yielded a new class of compounds to which we assigned tentatively the structure II or IIa.



II



IIa

Experimental

Diazocyclopentadiene.—A mixture of 20 g. of *p*-toluenesulfonyl azide, 8 ml. of freshly distilled cyclopentadiene, and 9 ml. of diethylamine was left at 0° for 3 days. The mixture slowly darkened and a precipitate formed. After adding 50 ml. of water, the mixture was extracted several times with pentane. The combined extracts were washed with water until they were almost neutral and then dried over sodium sulfate. The pentane extracts were concentrated by careful fractionation when necessary. When ethanolamine was used as the base, 0.5 hr. was found sufficient for the reaction time. The extracts could be washed neutral more easily, but the product was less pure.

(Cyclopentadienylhydrazono)triphenylphosphorane (I).—Triphenylphosphine (26 g.) in 100 ml. of ether was added to a solution of diazocyclopentadiene in pentane prepared from 20 g. of *p*-toluenesulfonyl azide, and after a short time an orange-red precipitate started to separate. After filtration and drying, 25.5 g. (73%) of I, m.p. 121–123° (from dichloromethane–hexane), was obtained. From other batches we obtained I melting at 149–150°.[6] The infrared spectra were identical with the spectra given by Ramirez and Levy[3] and by Bestmann and Gothlich.[7]

Anal. Calcd. for $C_{23}H_{19}N_2P$: C, 77.95; H, 5.40. Found: C, 78.09; H, 5.54.

(Indenylhydrazono)triphenylphosphorane.—A solution of diazoindene in pentane was prepared, using a similar procedure as described earlier, from 11.6 g. of indene, 19.7 g. of *p*-toluenesulfonyl azide, and 10 ml. of diethylamine. Addition of 26 g. of triphenylphosphine to this solution yielded 10 g. (25%) of a yellow precipitate, which after recrystallization from benzene melted at 159–160°.

Anal. Calcd. for $C_{27}H_{21}N_2P$: C, 80.18; H, 5.24; N, 6.93; P, 7.44. Found: C, 80.48; H, 5.41; N, 6.96; P, 7.44.

Infrared (KBr): 3030 (m), 1523 (s), 1476 (m), 1446 (m), 1430 (s), 1353 (m), 1308 (m), 1218 (s), 1092 (vs), 1050 (m), 1003 (vs), 992 (vs), 912 (m), 846 (m), 788 (s), 748 (s), 712 (s), 637 (s), 620 (m), 612 (m). The infrared spectrum in chloroform was essentially the same and did not show additional bands due to dissociation, as reported for I.[7]

II (R = Me).—Dimethyl phosphite (40 ml.) was added to a solution of diazocyclopentadiene prepared from 84 g. of *p*-toluenesulfonyl azide. An oil immediately separated and, after some time, crystallized. Recrystallization from chloroform–ether yielded 25 g. of II (R = Me), white crystals, m.p. 174–175°. From the mother liquid 8 g. more of the compound was isolated (total yield, 25%).

Anal. Calcd. for $C_7H_{11}N_2O_3P$: C, 41.61; H, 5.49; N, 13.87; P, 15.32. Found: C, 41.81; H, 5.73; N, 14.05; P, 15.36.

Infrared (KBr): 3160 (m), 3000 (w), 2945 (m), 2845 (w), 1680 (w), 1610 (w), 1430 (s), 1320 (w), 1232 (2), 1178 (m), 1020 (vs), 946 (w), 925 (m), 880 (w), 830 (m), 775 (m), 753 (m), 712 (w), 660 (w), 640 (w), 604 (w).

II. (R = Et).—This compound was prepared analogously to the methyl ester. It had a m.p. 177–178° (from ethyl acetate–hexane).

Anal. Calcd. for $C_9H_{15}N_2O_3P$: C, 46.96; H, 6.57; N, 12.17; P, 13.48. Found: C, 46.85; H, 6.43; N, 12.69; P, 13.69.

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(1) To whom inquiries should be directed.

(2) W. von E. Doering and C. H. DePuy, *J. Am. Chem. Soc.*, **75**, 5955 (1953).

(3) F. Ramirez and St. Levy, *J. Org. Chem.*, **23**, 2036 (1958).

(4) H. Staudinger and O. Kupfer, *Ber.*, **44**, 3197 (1911).

(5) H. Staudinger and J. Meyer, *Helv. Chim. Acta*, **2**, 619 (1919).

(6) Ramirez and Levy[3] reported a m.p. 121–122°, Bestmann and Gothlich[7] 151–153°. As we have observed both melting points it can be assumed that the compound exists in two modifications.

(7) H. J. Bestmann and L. Gothlich, *Ann.*, **656**, 1 (1962).