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# Preparation of Resonance-Stabilized Bisphosphoranes

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Five resonance-stabilized bisphosphoranes were prepared for the object of the future work. Preliminary examination was carried out in order to make clear the reactivity of the resonance-stabilized bisphosphoranes with the six aromatic monoaldehydes by the Wittig reaction. An unexpected ester exchange reaction of ethyleneglycol bischloroacetate (1) was discussed in the case of 9,6-dioxa-2,7-dioxoheptane-1,8-bistriphenylphosphonium chloride formation.

In our previous paper,[2] the synthesis of some oligopolymers by the Wittig reaction of aromatic *p*-substituted bisphosphoranes with aromatic bisaldehydes has been reported. In that process, the oligomerization was compelled to carry out by addition of ethanolic lithium ethoxide as a ylid-forming reagent to the mixtures of bisphosphonium salts such as *p*-xylylenebis(triphenylphosphonium chloride) and 2,5-dimethoxy-*p*-xylylenebis(triphenylphosphonium chloride), and of bisaldehydes such as terephthalaldehyde, 2-nitroterephthalaldehyde and 9,10-anthracenedicarboxaldehyde in the dimethylformamide solution, respectively, because those free bisphosphoranes were not isolable. Therefore, the resulting concentration of the bisphosphoranes in the reaction mixtures was regularly under control of the dropping rate of ylid-forming reagent (*i.e.* ethanolic lithium ethoxide solution), and so the oligomerization was always forced to proceed in the excess bisaldehydes.

Furthermore, the solubility of the each reactant in any solvent is one of outstanding factors to carry out smoothly the reaction. Especially, from our experiments, it seemed that lithium ethoxide using together as a Lewis base made more complicate the reaction mechanism.

When a resonance-stabilized bisphosphorne can directly be used as a starting material in stead of the corresponding bisphosphonium salt in order to avoid such complication, it may be more favorable for the oligomerization by the Wittig reaction. From the above reason, in this paper, synthesis of some resonance-stabilized bisphosphoranes as precursor of oligopolymer was attempted, and also preliminary observation of the behavior of the bisphosphoranes with some aromatic monoaldehydes in the Wittig reaction is necessary in order to work up our future works in this field.

The Wittig reaction has considerably been investigated from the stereospecific aspect.[3] It has been stated several times that the reaction is not stereospecific (see the Review[4]). At the same time, the control of the Wittig reaction to obtain either *cis* or *trans* isomer would be of considerable difficulty in synthesis of a bisolefin, as a fragment of oligopolymer, because the probability of formation of *cis* and *trans* in the reaction is strongly dependent upon the environmental conditions[3] and the constructions of the reactants.[5]

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1) Location: *Katakasu, Fukuoka.*
2) H. Saikachi and H. Mutō, *Chem. Pharm. Bull.* (Tokyo) **19**, 959 (1971).
3) *a*) L.D. Bergelson and M.M. Shemyakin, *Tetrahedron*, **19**, 149 (1963); *idem*, *Pure and Appl. Chem.*, **9**, 271 (1964); *idem*, *Angew. Chem.*, *Internat. Edn.*, **3**, 250 (1964); *b*) H.O. House, V.K. Jones and G.A. Frank, *J. Org. Chem.*, **29**, 3327 (1964); *c*) M. Schlosser and K.F. Christmann, *Ann.*, **708**, 1 (1967).
4) S. Trippett, "Advances in Organic Chemistry" Vol. 1, ed., by John Wiley and Sons, Inc., New York, N.Y., 1960, p. 83.
5) R. Ketcham, D. Jambotkar and L. Martinelli, *J. Org. Chem.*, **27**, 4666 (1962); H.O. House and G.H. Rasmusson, *ibid.*, **26**, 4278 (1961); A.W. Johnson and V.L. Kyllingstad, *ibid.*, **31**, 334 (1966); J.P. Snyder and H.J. Bestmann, *Tetrahedron Letters*, **38**, 3317 (1970).

Fortunately, it is well known that the yield of *trans*-olefination is generally superior to *cis*-olefination by using of the resonance-stabilized phosphorane under any environmental condition,6) and also the absence of a Lewis base (lithium ethoxide) in the reaction system promotes the formation of *trans* olefin.3a)

For the object of our work, all *trans* configulations are mostly favorable for the preparation of the desired linear oligopolymers.

In the present work, the synthesis of 2,5-dioxa-1,6-hexanebistriphenylphosphine methylene (**3**) as a resonance-stabilized bisphosphorane was attempted by Ford's method7) (Chart 1).

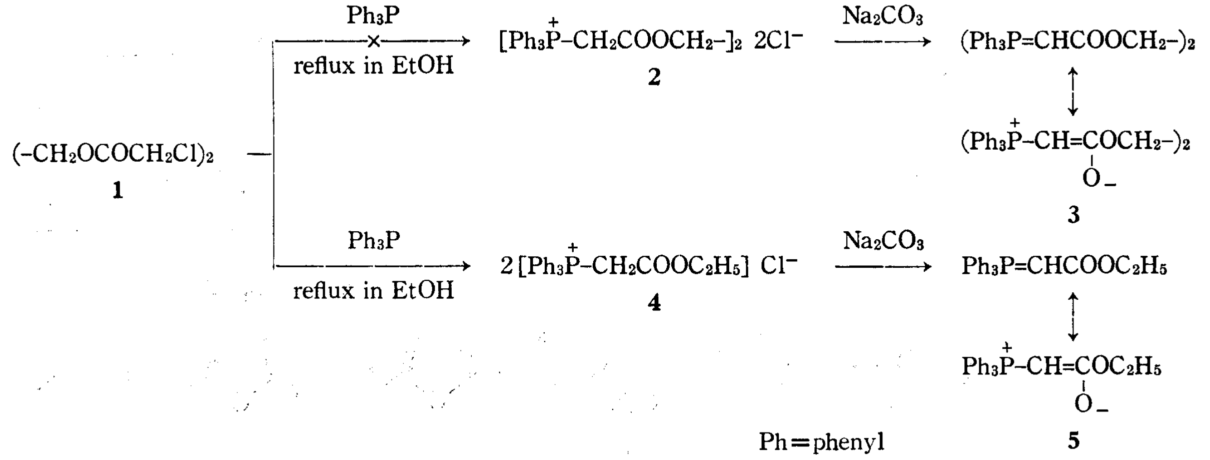

Chart 1

Unexpectedly, however, carboethoxymethylenetriphenylphosphorane (**5**)8) was formed in stead of **3**. Thus, a phosphonium salt (mp 130—133°) (**4**) obtained was proved to be identical with authentic carboethoxymethylenetriphenylphosphonium chloride9) (mp 130°) by mixed melting point determination. Furthermore, the infrared (IR) spectra and nuclear magnetic resonance (NMR) spectra (in $CDCl_3$) ($\delta$) of **4** and **5** are equal, respectively, *i.e.* 7.73 (15H, multiplet, aromatic protons), 5.46 (2H, doublet, $J=14.0$ cps, $\text{-C}\underline{\text{H}}_2\text{COOCH}_2\text{CH}_3$), 4.02 (2H, quartet, $J=7.0$ cps, $\text{-COOC}\underline{\text{H}}_2\text{CH}_3$) and 1.03 (3H, triplet, $J=7.0$ cps, $\text{-COOCH}_2\text{C}\underline{\text{H}}_3$). The above result occurred presumably due to the ester exchange with ethanol used as reaction solvent (Chart 1). Considering the above event, the synthesis of 9,6-dioxa-2,7-dioxoheptane-1,8-bistriphenylphosphonium chloride (**2**)7) was tried in other different organic solvents (benzene, chloroform, dimethylformamide) or without solvent to take off the above undesired ethanol effect, but every one led unexpectedly to unsuccess. It was suggested that the chemical properties of ethyleneglycol bischloroacetate (**1**) as a starting material might be responsible for the such undesired results (Chart 1). Therefore, we performed the synthesis of the resonance-stabilized bisphosphoranes possessing two triphenylphosphinecarbonylmethylene groups at the both opposite sides in the molecule (Chart 2).

As can be seen from Chart 2, 1,4-bisbromoacetylbenzene (**6a**) was given by the bromination of 1,4-diacetylbenzene10) in acetic acid.11) 4,4′-Bisbromoacetyldiphenyl (**6b**) was successfully, at one step, obtained by the modificated Friedel-Crafts reaction12) of diphenyl with

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6) A. Maercker, "Organic Reactions" Vol. 14, ed., by John Wiley and Sons, Inc., New York, N.Y., 1965, p. 313.
7) J.A. Ford and C.V. Wilson, *J. Org. Chem.*, **26**, 1433 (1961).
8) G. Witting and W. Haag, *Chem. Ber.*, **88**, 1654 (1955); O. Isler, H. Gutmann, M. Montavon, R. Rüegg, G. Ryser and P. Zeller, *Helv. Chim. Acta*, **40**, 1242 (1957).
9) G. Wittig and H. Pommer, Ger. Patent 943648 [*C.A.*, **52**, 16292d (1958)].
10) J.R. Holsten and E.H. Pitts, *J. Org. Chem.*, **26**, 4151 (1961).
11) P. Ruggli and E. Gassenmeier, *Helv. Chim. Acta*, **22**, 496 (1939).
12) *a*) L.M. Long and H.R. Henze, *J. Am. Chem. Soc.*, **63**, 1939 (1941); *b*) H. Schubert, H.J. Lorenz and R. Fischer, *J. Prakt. Chem.*, **22**, 140 (1963).

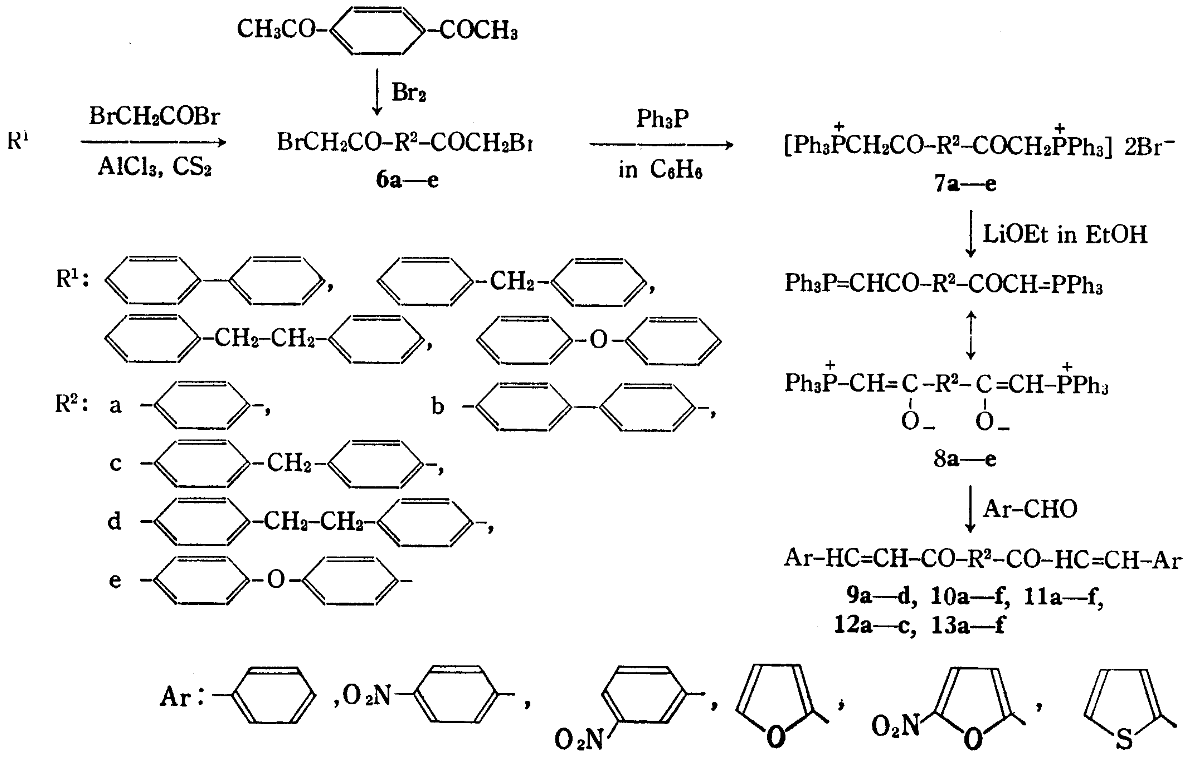
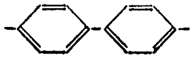
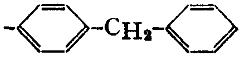
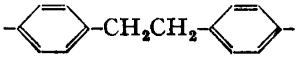
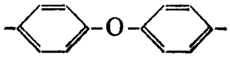


Chart 2

α-bromoacetylbromide[13] in dry carbon disulfide. Furthermore, other bromoacetylcompounds (**6c**—**e**) required were prepared from diphenylmethane, diphenylethane and diphenylether by the same as mentioned in **7a**, respectively (Table I).

Table I. Bisbromoacetyl Compounds $BrCH_2CO-R-COCH_2Br$

| No. | R | Appearance (Recryst. solvt.) | mp (°C) | Yield (%) | IR KBr (cm$^{-1}$) $\nu_{C=O}$ | Formula | Analysis (%) Calcd. C | Calcd. H | Found C | Found H |
|---|---|---|---|---|---|---|---|---|---|---|
| **6a** |  | colorless prisms (EtOH) | 179—180[a] | 63[b] | 1700 | $C_{10}H_8O_2Br_2$ | 37.54 | 2.52 | 37.59 | 2.63 |
| **6b** |  | pale yellow neeles (chloroform) | 230—231[c] | 38 | 1692 | $C_{16}H_{12}O_2Br_2$ | 48.52 | 3.05 | 48.64 | 3.18 |
| **6c** |  | pale yellow plates (benzene) | 142.5—143 | 43 | 1695 | $C_{17}H_{14}O_2Br_2$ | 49.79 | 3.44 | 49.97 | 3.66 |
| **6d** |  | pale yellow prisms (benzene) | 145.5—146.5 | 62 | 1671 | $C_{18}H_{16}O_2Br_2$ | 50.97 | 3.80 | 51.23 | 3.88 |
| **6e** |  | colorless plates (EtOH) | 124 | 55 | 1695 | $C_{16}H_{12}O_3Br_2$ | 46.64 | 2.94 | 47.46 | 3.07 |

*a*) lit.[11] mp 173°, lit.[12b] mp 181—182° *b*) calcd. on the basis of *p*-diacetylbenzene *c*) lit.[12b] mp 220—222°

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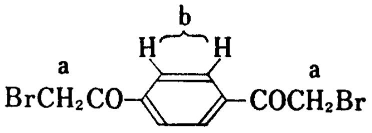
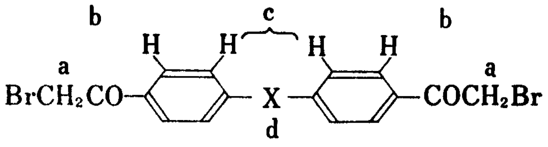
[13] K. Auwers and R. Bernhardi, *Chem. Ber.*, **24**, 2219 (1891).

TABLE II. Assignment of NMR spectra of Bisbromoacetyl Compounds



**6a**



**6b−e**

| No. | X | δ (ppm) in $CDCl_3$ Ha | Hb | Hc | Hd | $J^{a)}$ bc (cps) |
|---|---|---|---|---|---|---|
| **6a** | — | 4.45 (s) | 8.08 (s) | — | — | — |
| **6b** | — | 4.47 (s) | 8.11 (d)$^{a)}$ | 7.74 (d)$^{a)}$ | — | 9.0 |
| **6c** | $-CH_2-$ | 4.42 (s) | 7.92 (d)$^{a)}$ | 7.30 (d($^{a)}$ | 4.12 (s) | 8.5 |
| **6d** | $-CH_2CH_2-$ | 4.45 (s) | 7.91 (d)$^{a)}$ | 7.26 (d)$^{a)}$ | 3.05 (s) | 8.0 |
| **6e** | -O- | 4.44 (s) | 8.04 (d)$^{a)}$ | 7.12 (d)$^{a)}$ | — | 9.0 |

*a*) Seemingly to be AB pattern.

TABLE III. Bisphosphonium Salts

$[Ph_3\overset{+}{P}CH_2CO\text{-}R\text{-}COCH_2\overset{+}{P}Ph_3]2Br^-$

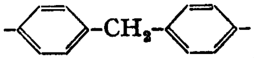
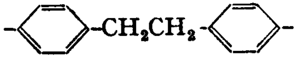
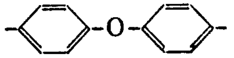
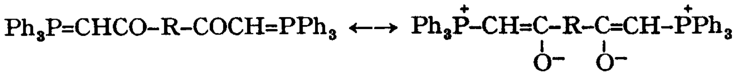
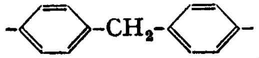
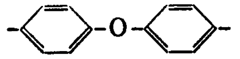
| No. | R | Yield (%) | mp (°C) (decomp.) | IR$_{KBr}$(cm$^{-1}$) | | Formula | Analysis (%) Calcd. | | Found | |
|---|---|---|---|---|---|---|---|---|---|---|
| | | | | $\nu_{Ph_3\overset{+}{P}-}$ | $\nu_{C=O}$ | | C | H | C | H |
| **7a** |  | 95 | 320—322 | 1107 | 1668 | $C_{46}H_{38}O_2P_2Br_2$ | 65.42 | 4.54 | 64.84 | 4.80 |
| **7b** |  | 87 | 292—294 | 1110 | 1661 | $C_{52}H_{42}O_2P_2Br_2$ | 67.84 | 4.60 | 67.57 | 4.83 |
| **7c** |  | 86 | 195—197 | 1110 | 1669 | $C_{53}H_{44}O_2P_2Br_2$ | 68.11 | 4.75 | 68.58 | 4.75 |
| **7d** |  | 84 | 181—184 | 1108 | 1666 | $C_{54}H_{46}O_2P_2Br_2$ | 68.40 | 4.89 | 68.72 | 5.14 |
| **7e** |  | 89 | 271—273 | 1109 | 1667 | $C_{52}H_{42}O_3P_2Br_2$ | 66.64 | 4.52 | 67.14 | 4.99 |

TABLE IV. Resonance Stabilized Bisphosphoranes

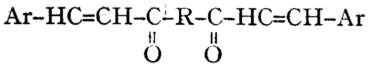


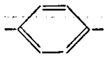
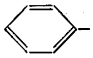
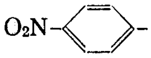
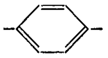
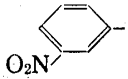
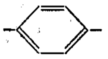
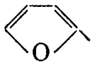
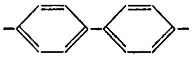
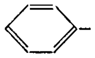
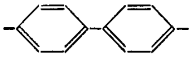
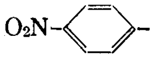
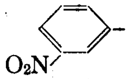
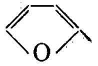
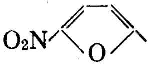
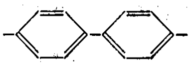
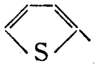
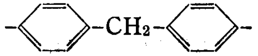
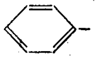
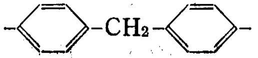
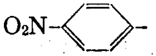
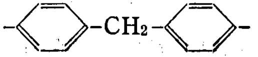
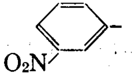
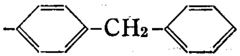
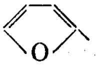
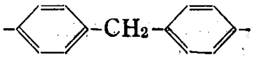
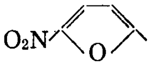
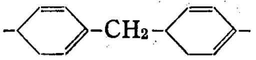
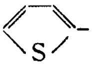
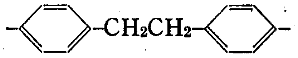
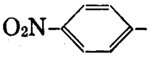
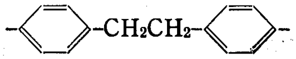
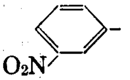
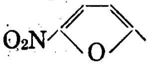
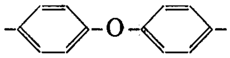
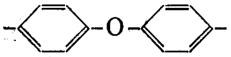
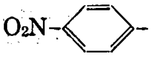
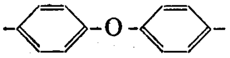
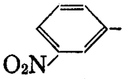
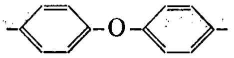
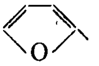
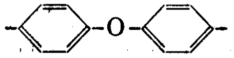
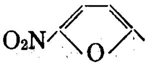
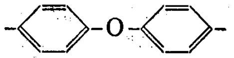
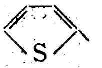
$$Ph_3P{=}CHCO\text{-}R\text{-}COCH{=}PPh_3 \longleftrightarrow Ph_3\overset{+}{P}\text{-}CH{=}\underset{O^-}{\underset{|}{C}}\text{-}R\text{-}\underset{O^-}{\underset{|}{C}}{=}CH\text{-}\overset{+}{P}Ph_3$$

| No. | R | Appearance (Recryst. solvt.) | Yield (%) | mp (°C) |
|---|---|---|---|---|
| **8a** |  | yellow prisms<br>(DMF) | 89 | 324—326 |
| **8b** |  | pale yellow prisms<br>(DMF+EtOH) | 88 | 290—293 |
| **8c** |  | pale yellow needles<br>(EtOH) | 81 | 296—299 |
| **8d** |  | colorless prisms<br>(DMF) | 85 | >340 |
| **8e** |  | colorless prisms<br>(EtOH) | 97 | 247—250 |

| No. | IR$_{KBr}$(cm$^{-1}$) | | Formula | Analysis (%) Calcd. | | Found | |
|---|---|---|---|---|---|---|---|
| | $\nu_{Ph_3P-}$ | $\nu_{C=O}$ | | C | H | C | H |
| **8a** | 1105 | 1521 | $C_{46}H_{36}O_2P_2$ | 80.92 | 5.32 | 80.95 | 5.43 |
| **8b** | 1103 | 1502 | $C_{52}H_{40}O_2P_2$ | 82.32 | 5.31 | 82.14 | 5.45 |
| **8c** | 1102 | 1510 | $C_{53}H_{42}O_2P_2$ | 82.37 | 5.48 | 82.11 | 5.71 |
| **8d** | 1102 | 1515 | $C_{54}H_{44}O_2P_2$ | 82.42 | 5.64 | 82.05 | 5.78 |
| **8e** | 1102 | 1495 | $C_{52}H_{40}O_3P_2$ | 80.61 | 5.22 | 80.85 | 5.44 |

TABLE V. Bisketovinyl Compounds


$\mathrm{Ar{-}HC{=}CH{-}}\underset{\substack{\| \\ \mathrm{O}}}{\mathrm{C}}\mathrm{{-}R{-}}\underset{\substack{\| \\ \mathrm{O}}}{\mathrm{C}}\mathrm{{-}HC{=}CH{-}Ar}$

| No. | R | Ar | Appearance (Recryst. solvt.) | Yield (%) |
|---|---|---|---|---|
| **9a** |  |  | pale yellow scales (EtOH) | 29a) |
| **9b** |  |  | pale yellow needles (DMF) | 98 |
| **9c** |  |  | pale yellow prisms (DMF) | 90 |
| **9d** |  |  | yellow needles (DMF) | 93 |
| **10a** |  |  | pale yellow plates (DMF) | 95 |
| **10b** |  |  | yellow prisms (DMF) | 96 |
| **10c** |  |  | pale yellow prisms (DMF) | 96 |
| **10d** |  |  | pale yellow prisms (DMF+$H_2O$) | 85 |
| **10e** |  |  | yellow scales (DMF+EtOH) | 92 |
| **10f** |  |  | yellow prisms (DMF+EtOH) | 81 |
| **11a** |  |  | colorless needles (EtOH) | 94 |
| **11b** |  |  | pale yellow prisms (DMF) | 96 |
| **11c** |  |  | pale yellow needles (DMF+EtOH) | 85 |
| **11d** |  |  | pale yellow needles (EtOH+$H_2O$) | 55 |
| **11e** |  |  | yellow needles (DMF+EtOH) | 96 |
| **11f** |  |  | yellow needles (EtOH) | 77 |
| **12a** |  |  | pale yellow prisms (DMF) | 96 |
| **12b** |  |  | pale yellow prisms (DMF) | 82 |
| **12c** |  |  | light brown prisms (DMF+EtOH) | 99 |
| **13a** |  |  | colorless scales (EtOH) | 72 |
| **13b** |  |  | colorless prisms (DMF+EtOH) | 96 |
| **13c** |  |  | pale yellow prisms (DMF+EtOH) | 85 |
| **13d** |  |  | pale yellow prisms (cyclohexane) | 81 |
| **13e** |  |  | yellow prisms (DMF+EtOH) | 96 |
| **13f** |  |  | pale yellow scales (EtOH) | 45 |

a) Dimethylformamide was used as a solvent.

| mp (°C) | $IR_{KBr}$ ($cm^{-1}$) |  | Formula | Analysis (%) |  |  |  |  |  |
|---|---|---|---|---|---|---|---|---|---|
|  | H C=C H | $\nu_{C=O}$ |  | Calcd. |  |  | Found |  |  |
|  |  |  |  | C | H | N | C | H | N |
| 217.5—219.5[b] | 983 | 1655 | $C_{24}H_{18}O_2$ | 85.18 | 5.36 | — | 85.01 | 5.39 | — |
| 330 —331[c] | 965, 976<br>987 | 1660 | $C_{24}H_{16}O_6N_2$ | 67.29 | 3.76 | 6.54 | 67.25 | 3.79 | 6.46 |
| 288 —289 | 975 | 1665 | $C_{24}H_{16}O_6N_2$ | 67.29 | 3.76 | 6.54 | 67.41 | 3.69 | 6.50 |
| >340 | 958, 969<br>985 | 1660 | $C_{20}H_{12}O_4N_4$ | 58.83 | 2.96 | 6.86 | 58.66 | 3.14 | 7.01 |
| 251 —252 | 985 | 1658 | $C_{30}H_{22}O_2$ | 86.93 | 5.35 | — | 86.83 | 5.45 | — |
| 340 —341 | 978, 980 | 1660 | $C_{30}H_{20}O_6N_2$ | 71.42 | 4.00 | 5.55 | 71.50 | 4.10 | 5.51 |
| 317 —318 | 980 | 1665 | $C_{30}H_{20}O_6N_2$ | 71.42 | 4.00 | 5.55 | 71.45 | 4.24 | 5.66 |
| 205 —208 | 970 | 1653 | $C_{26}H_{18}O_4$ | 79.17 | 4.60 | — | 78.83 | 4.66 | — |
| >340 | 957, 970<br>979 | 1660 | $C_{26}H_{16}O_4N_2$ | 64.46 | 3.33 | 5.78 | 64.18 | 3.66 | 5.89 |
| 231 —232 | 967 | 1649 | $C_{26}H_{18}O_2S_2$ | 73.21 | 4.25 | — | 73.32 | 4.32 | — |
| 166 —167 | 955, 988 | 1662 | $C_{31}H_{24}O_2$ | 86.89 | 5.65 | — | 86.70 | 5.79 | — |
| 259 —260 | 978, 984 | 1660 | $C_{31}H_{22}O_6N_2$ | 71.81 | 4.27 | 5.40 | 71.60 | 4.34 | 5.19 |
| 248 —249 | 983 | 1668 | $C_{31}H_{22}O_6N_2$ | 71.81 | 4.27 | 5.40 | 71.60 | 4.47 | 5.45 |
| 120 —121 | 975, 962 | 1654 | $C_{27}H_{20}O_4$ | 79.39 | 4.94 | — | 79.42 | 4.83 | — |
| 234 —235 | 970, 985 | 1666 | $C_{27}H_{20}O_8N_2$ | 65.06 | 3.64 | 5.62 | 64.92 | 3.64 | 5.62 |
| 161.5—162.5 | 955 | 1650 | $C_{27}H_{20}O_{21}S_2$ | 73.61 | 4.58 | — | 73.70 | 4.62 | — |
| 294 —296 | 985 | 1661 | $C_{32}H_{24}O_6N_2$ | 72.17 | 4.54 | 5.26 | 72.27 | 4.64 | 5.09 |
| 252.5—254.5 | 985 | 1660 | $C_{32}H_{24}O_6N_2$ | 72.17 | 4.54 | 5.26 | 72.02 | 4.75 | 5.35 |
| >340 | 972 | 1650 | $C_{28}H_{22}O_8N_2$ | 65.62 | 3.93 | 5.47 | 65.55 | 4.11 | 5.68 |
| 174 —175 | 975 | 1662 | $C_{30}H_{22}O_3$ | 83.70 | 5.15 | — | 83.77 | 5.26 | — |
| 224.5—225.5 | 967, 984 | 1663 | $C_{30}H_{20}O_7N_2$ | 69.22 | 3.87 | 5.38 | 69.45 | 3.88 | 5.35 |
| 212.5—214.5 | 975, 995 | 1669 | $C_{30}H_{20}O_7N_2$ | 69.22 | 3.87 | 5.38 | 69.36 | 4.01 | 5.24 |
| 144.5—146.5 | 963 | 1660 | $C_{26}H_{18}O_5$ | 76.09 | 4.42 | — | 76.19 | 4.68 | — |
| 205 —206 | 958, 975 | 1663 | $C_{26}H_{16}O_7N_2$ | 62.40 | 3.22 | 5.60 | 62.22 | 3.35 | 5.65 |
| 167.5—169 | 962 | 1655 | $C_{26}H_{18}O_3S_2$ | 70.56 | 4.10 | — | 70.70 | 4.09 | — |

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b) lit. mp 214° [S.V. Tsukerman, V. M. Nikitchenko, V.P. Maslennikova, V. E. Bondarenko and V. F. Lavrushin, *Khim. Geterotsikl. Soedin.*, **1968**(**6**), 1093; *C. A.*, **70**, 87653g (1969)] c) lit. mp 315° [idem., **ibid**]

It was confirmed on the basis of the NMR absorption (in $CDCl_3$) of aromatic protons which were shown in AA'XX' pattern (Table II) that the above four bisbromoacetyl compounds (**6b**—**e**) were 4,4'-bisbromoacetyl substituted series.

Second, bisphosphonium salts (**7a**—**e**) were prepared by addition of benzene solution of bisbromoacetyl compounds (**6a**—**e**) to a hot benzene solution of triphenylphosphine under reflux in good yield (Table III).

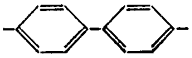
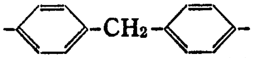
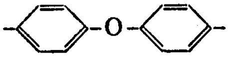
In order to yield the five desired resonance-stabilized bisphosphoranes (**8a**—**e**), the each corresponding bisphosphonium salt (**7a**—**e**), without purification, was carefully treated with ethanolic lithium ethoxide under nitrogen, and then five **8a**—**e** were obtained in good yield (Table IV). The elemental analytical data of these **8a**—**e** support the structures proposed in Chart 2, respectively (Table IV). Additionally, from IR spectra (KBr), it was suggested in terms of the striking shift[14)] of the carbonyl band in a lower frequency than that of the normal carbonyl groups and a characteristic band associated with tetravalent phosphorus (*ca.* 1105 $cm^{-1}$)[14b)] that the ylid linkage in those bisphosphoranes was stabilized by virtue of carbonyl group[7)] (Table IV).

In this work, the behavior of the resonance-stabilized **8a**—**e** in the Wittig reaction was preliminarily examined by action with the aromatic monoaldehydes such as benzaldehyde, *p*-nitrobenzaldehyde, *m*-nitrobenzaldehyde, furfural, 5-nitrofurfural and 2-formylthiophene for the benifit of next work (see Table V). The examinations resulted all in good yield except **8a** and **8d** which were mostly unchanged with nitro-unsubstituted aromatic aldehydes. Consequently, it was suggested that the nitro group (electron withdrawing group) played an important role to make the aldehyde group active in the Wittig reaction, although the poor solubility of the every reactant in benzene is greatly responsible for the inhibiting of the reaction. The elemental analytical and IR spectral data of all bisketovinyl compounds obtained are given in Table V.

In the IR spectra (in KBr), a characteristic band associated with tetravalent phosphorus (*ca.* 1105 $cm^{-1}$)[14b)] was not found out, but carbonyl band at ordinary frequency (*ca.* 1660 $cm^{-1}$). Furthermore, the configuration of these bisketovinyl compounds may be estimated to be *trans, trans* configuration by the IR spectral band associated with *trans*-1,2-disubstituted

TABLE VI. Bisglyocalyl Compounds

$OHCCO\text{-}R\text{-}COCHO \cdot nH_2O$

| No. | R | Appearance | mp (C°) | Yield (%) | $IR_{KBr}$ ($cm^{-1}$) $\nu_{COCHO}$ | Analysis (%) Calcd.[a)] C | H | Found C | H | n |
|---|---|---|---|---|---|---|---|---|---|---|
| **14a** |  | colorless prisms | 144—147[b)] | 40 | 1695 | 53.10 | 4.46 | 53.01 | 4.56 | 2 |
| **14b** |  | pale yellow cryst. powder | 150[c)] | 49 | 1690 | 63.57 | 4.67 | 64.25 | 4.59 | 2 |
| **14c** |  | white prisms | 102—104 | 42 | 1690 | 70.58 | 4.53 | 69.59 | 4.91 | 0.5 |
| **14d** |  | white cryst powder | 122—125[d)] | 61 | 1690 | 67.28 | 5.33 | 67.10 | 5.41 | 1.5 |
| **14e** |  | white prisms | 124—127[e)] | 45 | 1690 | 64.00 | 4.03 | 63.87 | 4.13 | 1 |

a) calcd. for hydrate b) lit.[11)] mp 110—111°, lit.[13b)] mp 138—158° c) lit.[13b)] mp 130—145° *d*) lit.[16)] mp 147—149° *e*) lit.[16)] mp 147—149°

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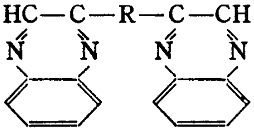
14) *a*) F. Ramirez and S. Dershowitz, *J. Org. Chem.*, **22**, 41 (1957); *b*) A.J. Speziale and K.W. Ratts, *J. Org. Chem.*, **28**, 465 (1963).

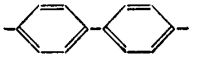
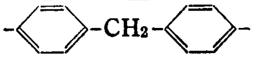
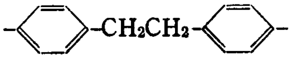
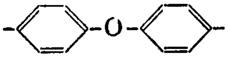
olefin (*ca.* 970 cm$^{-1}$)[15] and by the stability for thermodynamical treatment.[16] The NMR spectral patterns of these bisketovinyl compounds (**9**—**13**) were too complicate to assign.

Finally, the five available bisbromoacetyl compounds (**6a**—**e**) in our laboratory were submitted to the dimethylsulfoxide oxidation process[17] to prepare the corresponding bisglyoxalyl compounds (**14a**—**e**) as important component for the oligomerization by the Wittig reaction, although there are other methods[11,12b,18] for the formation of the bisglyoxalyl compounds (Table VI).

Then, these glyoxalyl compounds obtained were identified by the formation of quinoxaline derivatives (**15a**—**e**) with *o*-phenylenediamine in quantitative yield, respectively (Table VII).

TABLE VII. Bisquinoxaline Derivatives



| No. | R | Appearance (Recryst. solvt.) | mp (°C) | Formula | Analusis (%) Calcd. C | H | N | Found C | H | N |
|---|---|---|---|---|---|---|---|---|---|---|
| **15a** |  | pale yellow needles (DMF+EtOH) | 274—275[a] | $C_{22}H_{14}N_4$ | 79.02 | 4.22 | 16.77 | 78.90 | 4.22 | 16.78 |
| **15b** |  | pale yellow needles (DMF) | 268—270[b] | $C_{28}H_{18}N_4$ | 81.93 | 4.42 | 13.65 | 81.91 | 4.39 | 13.73 |
| **15c** |  | pale yellow needles (EtOH+DMF) | 222—223[c] | $C_{29}H_{20}N_4$ | 82.05 | 4.75 | 13.20 | 81.77 | 4.68 | 13.22 |
| **15d** |  | light grey plates (EtOH+DMF) | 210.5—211.5 | $C_{30}H_{22}N_4$ | 82.16 | 5.06 | 12.78 | 82.37 | 5.11 | 12.76 |
| **15e** |  | pale yellow prisms (EtOH) | 176—177 | $C_{28}H_{18}ON_4$ | 78.85 | 4.25 | 13.14 | 78.82 | 4.42 | 12.97 |

*a*) lit.[11] mp 262°, lit.[12b] mp 272.5—273.5° *b*) lit.[12b] mp 266—268° *c*) lit.[18] mp 214°

## Experimental[19]

**4,4′-Bisbromoacetyl Compounds (6b—e)**——General Method: 80 g (0.6 mole) of anhydrous aluminium chloride was suspended in about 100 ml of dry carbon disulfide in a three-neck 500 ml round-bottom flask fitted with a reflux condenser, an oil-sealed mechanical stirrer and a dropping funnel. Mixture of 28.8 g (0.2 mole) of diphenyl and 121.1 g (0.6 mole) of α-bromoacetyl bromide[13] in dry carbon disulfide was added to the rappidly stirred suspension over a period of forty minutes at room temperature. Stirring was continued for thirty minutes after addition was complete, and then reaction mixture was refluxed on a water bath for four hours. Carbon disulfide was removed by distillation and sirupy residue was hydrolyzed by adding it to 1 liter of ice water contained hydrochloric acid. Precipitate formed was filtered, and washed with a small amount of ether. The crude product was recrystallized from chloroform using activated carbon to give 30 g (38%) of pure 4,4′-bisbromoacetyldiphenyl (**6a**).

The other bisbromoacetyl compounds (**6c**—**e**) were also prepared by the same way.

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[15] L.J. Bellamy, "The Infrared Spectra of Complex Molecules" 2nd ed. by John Wiley and Sons, Inc., New York, 1958, 34, 45—49.

[16] T.W. Campbell and R.N. McDonald, *J. Org. Chem.*, **24**, 1246 (1959).

[17] N. Kornblum, J.W. Powers, G.J. Anderson, W.J. Jones, H.O. Larson, O. Levand and W.M. Weaver, *J. Am. Chem. Soc.*, **79**, 6562 (1957).

[18] J.K. Stille and J.R. Williamson, *J. Polymer Sci.*, **A2**, 3867 (1964); G. Cavallini and E. Massarani, Brit. Patent 925445 (1963) [*C.A.* **59**, 13886d (1963)].

[19] *a*) All melting points were not corrected; *b*) The IR spectrometer used in this work was Nihonbunko Model-DS301 infrared spectrophotometer.

Appearance, melting points, carbonyl absorption band and elemental analytical data were listed in Table I. Assignments of NMR spectra were shown in Table II.

**Bisphosphonium Salts (7a—e)**——As a general method, to a stirred solution of triphenylphosphine (0.05 mole) in dry benzene (200 ml), a dilute benzene solution of **6a—e** (0.02 mole) was carefully added dropwise under reflux. After addition was complete, stirring and refluxing were continued for several hours. The white precipitate formed was filtered, washed with dry benzene several times, followed by dry ether and dried in vacuum desiccator to give crude bisphosphonium salt. The crude product was pure enough for the synthesis of bisphosphoranes (**8a**—**e**).

Yield and analytical data were listed in Table III.

**Resonance-Stabilized Bisphosphoranes (8a—e)**——As a general method, a solution of 0.15 g (0.02 g. atom) of lithium dissolved in ethanol (50 ml) was added dropwise to a stirring solution of 0.01 mole of bis-triphenylphosphonium salt (**7a—e**) in absolute ethanol (200 ml) under nitrogen at room temperature. Stirring was continued after addition, and reaction mixture was cooled on an ice bath to give fairly pure bisphosphorane.

Analytical sample was recrystallized from organic solvents mentioned in Table IV. Appearance, yield and analytical data were listed in Table IV.

**Reaction of Resonance-Stabilized Bisphosphoranes (8a—e) with Aromatic Monoaldehydes**——General Method: A solution of aromatic monoaldehyde (0.005 mole)(see Table V) and bisphosphorane (0.005 mole) in dry benzene (70 ml) was refluxed for 24 hr, solvent removed under reduced pressure and the residue was extracted with ethanol to take off a triphenylphosphine oxide. The residue was several times recrystallized from organic solvent mentioned in Table V to give pure bisketovinyl compound.

Appearance, yield and analytical data were shown in Tavle V.

**Bisglyoxalyl Compounds (14a—e)**——As a general method, a solution of bisbromoacetyl compound (see Table I) in dimethylsulfoxide (20 ml) was allowed to stand at room temperature for 24 hr. The reaction mixture was poured into ice water, stirred one hr and white precipitate formed was collected by suction. Recrystallization of this precipitate from water gave a bisglyoxalyl compound as a hydrate.

Appearance, yield and analytical data were listed in Table VI.

**Bisquinoxaline Derivatives (15a—e)**——General Method: A solution of *o*-phenylenediamine (0.005 mole) and bisglyoxalyl compounds (0.005 mole) in ethanol was refluxed for thirty minutes to give crude bisquinoxaline derivatives in quantitative yield. The crude product was recrystallized from ethanol, ethanol–dimethylformamide mixture or dimethylformamide, respectively.

Appearance and analytical data were listed in Table VII.

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