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SYNTHESIS OF 1,4-DIENES AND α-ALKOXYSTYRENE DERIVATIVES VIA ALLYL- AND BENZYLBORONATION OF ACETYLENIC COMPOUNDS

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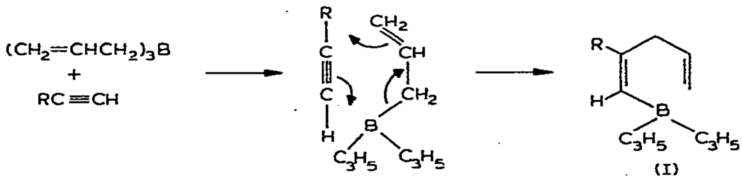
SUMMARY

The addition of allylboranes to monosubstituted acetylenic compounds followed by protolysis of the resulting vinylboranes is a general method for synthesis of 1,4-substituted pentadienes.

α-Alkoksystyrenes are obtained via the reaction of benzylboranes with alkoxyacetylenes.

The reaction of triallylborane with acetylene and its derivatives (allylboron–acetylene condensation) leading to 3-borabicyclo[3.3.1]non-6-ene derivatives[1-7] involves three consequent stages[3-5,8-11].

The first stage of this condensation is *cis*-addition of the allylboron fragment of allylborane molecule to the triple bond of the acetylenic compound[3,5,8,10,11], which occurs with allyl rearrangement[12,13].



(I)

[R = H, D, alkyl, RO, $CH_2{=}CH$, C_6H_5, $(CH_3)_3Si$; C_3H_5 = allyl]

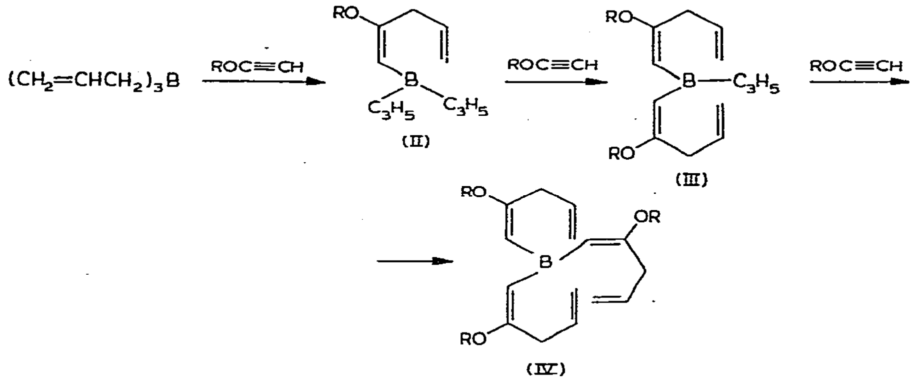
The boron atom and the substituent R are *trans*-situated at double bond in the compounds of type (I).

The addition of triallylborane to monosubstituted acetylenes occurs at room temperature or on cooling depending upon the nature of R.

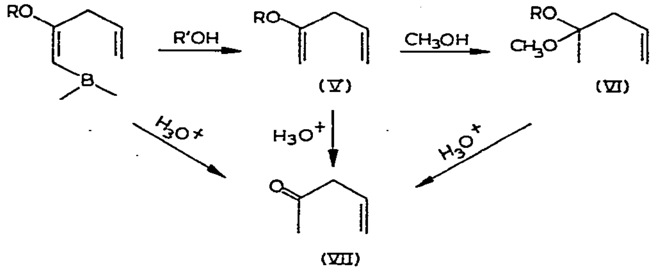
The vinylboranes of type (I) may be used to prepare 2-substituted 1,4-pentadienes and some of their derivatives.

The interaction of triallylborane with alkoxyacetylenes (proceeding at −50–20° and being dependent on the ratio of reagents) results in (*trans*-2-alkoxy-1,4-pentadienyl)diallylborane (II), bis(*trans*-2-alkoxy-1,4-pentadienyl)allylborane (III) or tris(*trans*-2-alkoxy-1,4-pentadienyl)borane (IV) with 85, 80 and 65% yield, respectively.

The reaction should be performed in an inert solvent (such as isopentane) by adding the solution of the alkoxyacetylene to a cooled solution of triallylborane (—70–40°) followed by heating of the reaction mixture to room temperature.



The B–sp^2C bond of these compounds [(II)–(IV)] can be readily cleaved by alcohols, water and bases at 20–100° yielding 2-alkoxy-1,4-pentadienes (V).



(R = CH_3, C_2H_5; R' = alkyl)

In the case of tris(2-alkoxy-1,4-pentadienyl)boranes (IV) only two B–C bonds are readily splitted by the action of alcohols (20–100°). Protolysis of the third B–C bond hardly occurred on prolonged heating with alcohols. Quantitative yields of 2-alkoxy-1,4-pentadienes (V) are obtained by alcoholysis of unsymmetrical boranes [(II) and (III), one mole of (III) giving rise to two moles of diene][8,10,14]. The mechanism of the alcoholysis of (*trans*-2-alkoxyvinyl)boranes has been reported in a previous communication[14].

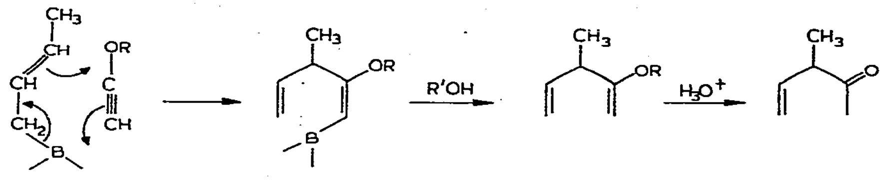
The use of higher alcohols for alcoholysis is more convenient for the simultaneous distillation of the diene (V) from the reaction mixture.

The prolonged heating of the boranes of type (II)–(IV) with alcohols gives rise to ketals of methyl allyl ketone. Thus methyl ethyl ketal of methyl allyl ketone (VI) has been obtained by refluxing compound (II) or (IV) ($R{=}C_2H_5$) in methanol.

The acid hydrolysis of vinylboranes [(II)–(IV)] as well as of the compounds of type (V) and (VI) yields methyl allyl ketone (VII) identified as its 2,4-dinitrophenylhydrazone. It should be pointed out that pure methyl allyl ketone (VII) can be obtained by hydrolysis using 1% solution of hydrochloric acid; the use of more concentrated solution of HCl results in a mixture containing (VII) and methyl *trans*-

propenyl ketone, the proportion of the latter in the mixture increases with increasing acid concentration [acid isomerization of (VII) into conjugated ketone].

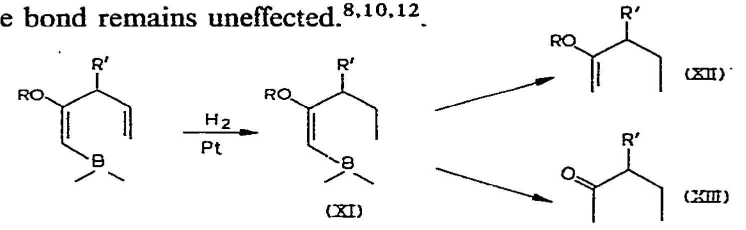
The interaction of 2-butenyl derivatives of boron [such as 1-(2-butenyl)-boracyclopentane and tri(2-butenyl)borane] with ethoxyacetylene gives (2-ethoxy-3-methyl-1,4-pentadienyl)boranes (VIII) through allyl rearrangement[13] which quantitatively yield 2-ethoxy-3-methyl-1,4-pentadiene (IX) after alcoholysis.



(VIII) (IX) (X)

Compound (IX) was found to be free from any 2-butenyl derivative (established by gas chromatography) and in acid hydrolysis gave 3-methyl-4-penten-2-one (X) identified as its 2,4-dinitrophenylhydrazone.

The terminal and non-terminal double bonds of the diene compounds of boron [(II)–(IV), (VIII)] behave quite differently on catalytic hydrogenolysis. Terminal double bonds are hydrogenated over technical Pt-black whereas the other double bond remains uneffected.[8,10,12]

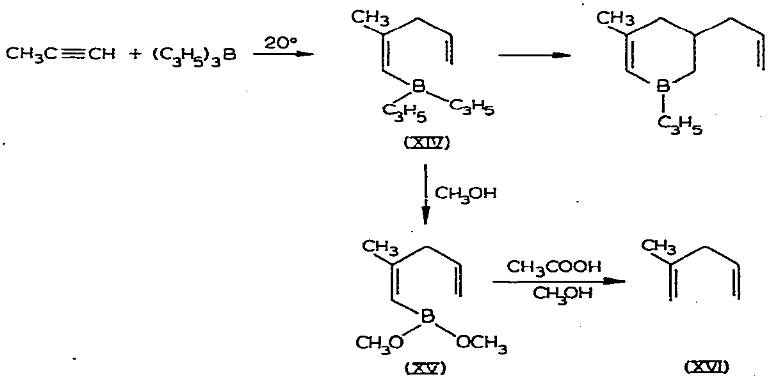


(XI) (XII) (XIII)

(R = CH_3, C_2H_5; R′ = H, CH_3)

The vinylboranes (XI) obtained by hydrogenation yield vinylic ethers (XII) after alcoholysis and corresponding ketones (XIII) on acid hydrolysis.

The alkylacetylenes quite differently from alkoxyacetylenes react very slowly with triallylborane at 20° (from 20 h to 2 or 3 days) yielding only mono-addition products [(I) or (XIV)] which undergo slow cyclization to give 3-alkyl-1,5-diallyl-1-bora-2-cyclohexenes[3,5,9,11].

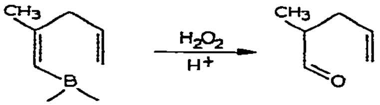


(XIV) (XV) (XVI)

Similar reaction with n-butylacetylene has been described earlier[5,11].

It is of interest to note that the boron–vinyl bond in the product (XIV) is much more stable to alcoholysis than that in corresponding 2-alkoxy derivatives [(II)–(IV)]. Because of this difference the reaction of borane (XIV) with an alcohol gives esters of (2-methyl-1,4-pentadienyl)boronic acid (XV) with the elimination of two moles of propylene. The compounds (XIV) and (XV) give 2-methyl-1,4-pentadiene (XVI) in 78% yield on heating at 80–100° with organic acids or with a mixture of methanol and acetic acid (in the last case the solvolysis occurs considerably faster).

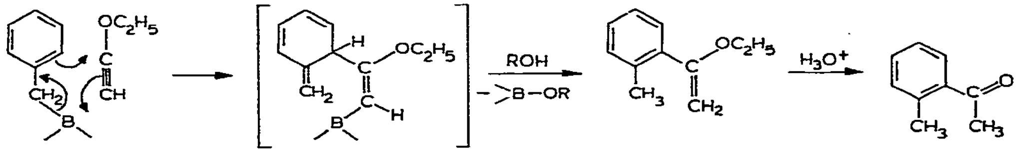
The oxidation of (XIV) or (XV) by hydrogen peroxide in acidic medium yields 2-methyl-4-penten-1-al (XVI) identified as its 2,4-dinitrophenylhydrazone.



(XVII)

Thus carboboronation of mono-substituted acetylenic compounds using allylboranes followed by protolysis of the obtained vinylboranes [(I)–(IV), (VIII), (XI), (XIV), (XV)] seems to be a general method for the synthesis of difficultly obtainable 1,4-substituted pentadienes.

Benzyl derivatives were found to be quite similar to allyl compounds. Thus the reaction of tribenzylborane with ethoxyacetylene in ether, THF, isopentane or without any solvent gave the tolyl derivative and not the benzyl derivative of the type $R_2BCH{=}C(OC_2H_5)CH_2C_6H_5$ indicating the process of organoboronation to occur with allyl rearrangement[12,13].



(XVIII) (XIX) (XX)

The formation of 1-ethoxy-1-*o*-tolylethylene (XIX) obtained by ethanolysis of the product of the reaction of tribenzylborane with ethoxyacetylene (in ratio 1/1 and 1/2) is due to the protolytic fission of boron–vinyl bond. The acid hydrolysis of vinyl ether (XIX) gave *o*-methylacetophenone (XX).

The structure of 1,4-dienes [(V), (IX), (XVI)], ketal (VI), ketone (VII) as well as of vinyl ethers of type (XII) and (XIX) is confirmed by IR and PMR spectra (Table 1). The melting points of 2,4-dinitrophenylhydrazones of the carbonyl compounds obtained in this work are listed in Table 2.

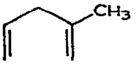
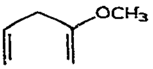
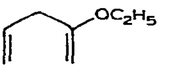
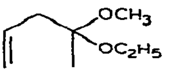
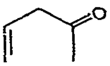
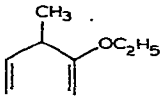
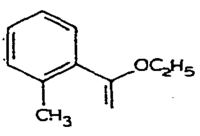
EXPERIMENTAL

General comments

All reactions of organoboron compounds and alkoxy-1,4-pentadienes were performed under an atmosphere of dry argon.

Triallylborane, b.p. 51–52° (20 mm), was prepared from allylbromide, alumi-

TABLE 1

Compound	B.p. [°C (mm)]	n_D^{20}	IR spectra (cm^{-1})	PMR spectra (δ, ppm)[a]
	57–58 (746)	1.4067	1646, 1655 (sh), 1790, 1833, 3008, 3081	1.65 (CH_3, 3 H), 2.67 (d, J 7 Hz, $=C{-}CH_2{-}C=$, 2 H), 4.66 ($CH_2{=}C\genfrac{}{}{0pt}{}{C}{C}$, 2 H), 4.70–5.18 (m, $CH_2{=}C\genfrac{}{}{0pt}{}{C}{C}$, 2 H), 5.38–6.07 (m, $C{=}CH{-}C$, 1 H)
	45–46 (130)	1.4257	1608, 1645, 1660, 1810, 3004, 3080, 3118	2.77 (d, J 7 Hz, $=C{-}CH_2{-}C=$, 2 H), 3.42 (s, $CH_3{-}O$, 3 H), 3.82 ($CH_2{=}C{-}O$, 2 H), 4.80–5.23 (m, $CH_2{=}C\genfrac{}{}{0pt}{}{C}{C}$ 2 H), 5.50–6.25 (m, $C{=}CH{-}C$, 1 H)
	54.2–54.3 (100)	1.4299	1604, 1646, 1661, 3010, 3080, 3120	1.25 (t, J 7 Hz, $CH_3{-}C{-}O$, 3 H), 2.75 (d, J 7 Hz, $=C{-}CH_2{-}C=$, 2 H), 3.78 ($CH_2{=}C\genfrac{}{}{0pt}{}{O}{C}$, 2 H), 3.63 (q, J 7 Hz, $CH_2{-}O$, 2 H), 4.85–5.38 (m, $CH_2{=}C\genfrac{}{}{0pt}{}{C}{C}$, 2 H), 5.47–6.22 (m, $C{=}CH{-}C$, 1 H)
	36–38 (15) 60–62 (44)	1.4152	1647, 3008, 3080	1.08 (t, $CH_3{-}C\genfrac{}{}{0pt}{}{O}{O}C$, 3 H), 1.15 (s, $CH_3{-}C{-}O$, 3 H), 2.32 (d, $=C{-}CH_2{-}C=$, 2 H), 3.08 (s, $CH_3{-}O$, 3 H), 3.38 (q, $O{-}CH_2{-}C$, 2 H), 4.72–5.18 (m, $CH_2{=}C$, 2 H), 5.35–6.22 (m, $C{=}CH{-}C$, 1 H)
	56–57 (130)	1.4145	1646, 1728, 1850, 3008, 3087	2.05 (s, CH_3, 3 H), 3.12 (d, J 7 Hz, $CH_2{-}C=$, 2 H), 4.85–5.20 (m, $CH_2{=}C$, 2 H), 5.50–6.25 (m, $C{=}CH{-}C$, 1 H)
	70–70.5 (120)	1.4262	1605, 1645 (sh), 1655, 1833, 3080, 3120	1.13 (d, J 7 Hz, $CH_3{-}C\genfrac{}{}{0pt}{}{C}{C}$), 3 H), 1.24 (t, J 7 Hz, $CH_3{-}C{-}O$, 3 H), 2.50 (d–q, $=C{-}CH{-}C=$, 1 H), 3.67 (q, J 7 Hz, CH_2O, 2 H), 3.82 ($CH_2{=}C\genfrac{}{}{0pt}{}{O}{C}$, 2 H), 4.75–5.22 (m, $CH_2{=}C{-}C$, 2 H), 5.43–6.10 (m, $C{=}CH{-}C$, 1 H)
	81–82 (8)	1.5141	1580 (sh), 1610, 1650, 3023, 3066, 3101, 3122	1.25 (t, J 7 Hz, $CH_3{-}C{-}O$, 3 H), 2.25 (s, $CH_3{-}Ar$, 3 H), 3.70 (q, J 7 Hz, $CH_2{-}O$, 2 H), 4.03, 4.13 (two d, J 2 Hz, $CH_2{=}C$, 2 H), 6.85–7.25 (m, C_6H_4, 4 H)[b]

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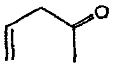
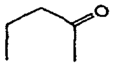
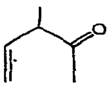
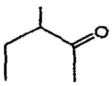
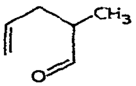
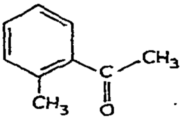
[a] Downfield from TMS; m = multiplet, s = singlet, d = doublet, t = triplet, q = quartet. [b] In CCl_4 solution (25%).

TABLE 2

2,4-DINITROPHENYLHYDRAZONES

Carbonyl compound	Empirical formula of hydrazone	M.p. (°C) of hydrazones		Analysis found (calcd.) (%)		
		Observed	Lit. data (ref.)	C	H	N
	$C_{11}H_{12}N_4O_4$	157.5–158.5	157 (15)	50.45 (50.00)	4.80 (4.58)	21.98 (21.20)
	$C_{11}H_{14}N_4O_4$	144–145	144 (16)	49.76 (49.63)	5.34 (5.30)	21.21 (21.04)
	$C_{12}H_{14}N_4O_4$	84–86	80 (17)	51.63 (51.79)	5.05 (5.07)	
	$C_{12}H_{16}N_4O_4$	74.2–74.5	73 (18)	51.40 (51.42)	5.71 (5.75)	
	$C_{12}H_{14}N_4O_4$	102–103	98 (19) 104–105 (20)	51.78 (51.79)	4.90 (5.07)	
	$C_{15}H_{14}N_4O_4$	167.5–168	164–166 (21)	57.29 (57.32)	4.40 (4.49)	

nium and n-butyl borate[22]. 1-(2-Butenyl)boracyclopentane, b.p. 41–41.2° (15 mm), n_D^{20} 1.4490, was prepared from 2-butenyl bromide and 1-butoxyboracyclopentane under analogous conditions[23].

Methoxyacetylene, b.p. 22°, and ethoxyacetylene, b.p. 51–52°, were prepared from the corresponding vinyl ethers following the known method[24].

The compounds of type (II)–(III) ($R = CH_3$, C_2H_5) and (VIII) were synthesized from the corresponding allylboranes and alkoxyacetylenes at −70–20° [8,10,12,14].

To prepare 2,4-dinitrophenylhydrazones a solution containing 2 g of 2,4-dinitrophenylhydrazine, 15 ml of H_2SO_4, 50 ml of H_2O and 100 ml of CH_3OH was used.

2-Methoxy-1,4-pentadiene [*(V)* $R=CH_3$]

To 11.0 g of bis(2-methoxy-1,4-pentadienyl)allylborane [(III), $R=CH_3$], b.p. 92–93° (1 mm) n_D^{20} 1.5081, d_4^{20} 0.9221[10], in a Favorsky flask was added dropwise 24 ml of n-nonanol. The temperature being kept at 20°. Distallation (bath-temperature 20–180°) gave 8.12 g (91.8%) of 2-methoxy-1,4-pentadiene [(V), $R=CH_3$], b.p. 45–46° (130 mm). (Found: C, 73.10; H, 10.01. $C_6H_{10}O$ calcd.: C, 73.43; H, 10.27%.)

The compound (V) ($R=CH_3$) was obtained by a similar procedure starting with tris(2-methoxy-1,4-pentadienyl)borane [(IV), $R=CH_3$][10].

2-Ethoxy-1,4-pentadiene [(*V*), *$R=C_2H_5$*]

A similar procedure starting with 17 g of bis(2-ethoxy-1,4-pentadienyl)-allylborane [(III), $R=C_2H_5$], b.p. 95.5–97° (2 mm), n_D^{20} 1.5050, d_4^{20} 0.9012[10], gave compound (V) [13.1 g (87.1%), b.p. 48–50° (90 mm)]. (Found: C, 74.98; H, 10.40. $C_7H_{12}O$ calcd: C, 74.95; H, 10.79%.)] It was also prepared from tris(2-ethoxy-1,4-pentadienyl)borane [(IV), $R=C_2H_5$)][10].

2-Ethoxy-3-methyl-1,4-pentadiene (*IX*)

Reaction between 9.5 g of 1-(2-ethoxy-3-methyl-1,4-pentadienyl)boracyclopentane [(VIII), b.p. 61–61.5° (2.5 mm), $n_D^{20.5}$ 1.4810[13]] and 8.7 g of n-nonanol gave 6.15 g (98.7%) of (IX), b.p. 50° (50 mm). (Found: C, 76.16; H, 11.32. $C_8H_{14}O$ calcd.: C, 76.14; H, 11.18%.)

Methyl ethyl ketal of methyl allyl ketone (*V*)

(1). From (2-ethoxy-1,4-pentadienyl)diallyborane [(II), $R=C_2H_5$], b.p. 65–66° (3 mm), n_D^{20} 1.4885, d_4^{20} 0.856[10].

To 16.1 g of (II) ($R=C_2H_5$) in a two-necked flask equipped with a dropping funnel and a condenser was added 10 ml of abs. methanol at 0°. Evolution of propylene was observed. The mixture was refluxed for 10 h, treated with 0.1 *N* NaOH (three times) and dist. H_2O. Upper (organic) layer was dried over K_2CO_3. Distillation gave 7.5 g (77.8%) of ketal (VI), b.p. 36–38° (15 mm). (Found: C, 66.20; H, 11.10. $C_8H_{16}O_2$ calcd.: C, 66.63; H, 11.19%.)

(2). From tris(2-ethoxy-1,4-pentadienyl)borane [(IV), $R=C_2H_5$, b.p. 137–139° (0.5 mm), n_D^{20} 1.5210, d_4^{20} 0.9446][10].

A mixture of 5.45 g of (IV) and 7 ml of CH_3OH was kept for three weeks. The completion of reaction was checked by disappearance of an absorption band characteristic of the $>B-CH=C<$ double bond (1580 or 1612 cm^{-1}) in the IR spectrum of the reaction mixture. The latter was shaken several times with 0.1 *N* NaOH and dist. H_2O (portions 5 ml). The organic layer was dried over K_2CO_3. Distillation gave 2.65 g (50%) of ketal (VI), b.p. 60–62° (44 mm), which contained 3% of impurities (GLC).

Methyl allyl ketone (*VII*)

A cooled mixture of 20.3 g of 2-ethoxy-1,4-pentadiene [(V), $R=C_2H_5$] and 10 ml of 1% HCl was stirred vigorously for 15 min. After the mixture became homogeneous the solution was extracted with n-decane (4×20 ml) and dried over K_2CO_3 and $MgSO_4$. Distillation gave 8.94 g of pure methyl allyl ketone (VII) (GLC, PMR), b.p. 56.5–57° (130 mm), n_D^{20} 1.4145.

2,4-Dinitrophenylhydrazone of methyl allyl ketone (*VII*)

To a stirred solution of 0.6 g of (IV) ($R=C_2H_5$) in 10 ml of CH_3OH was added 80 ml of a solution of 2,4-DNPH. After a period of 2 h the formed precipitate was filtered, washed with water and 30% methanol and chromatographed on a column with alumina (methanol/hexane). After crystallization the hydrazone had m.p. 157.5–158.5°. The same hydrazone was obtained using identical procedure from compounds (II), (III), (V)–(VII).

The other 2,4-dinitrophenylhydrazones (Table 2) were obtained as described above.

2-*Methyl*-1,4-*pentadiene* (*XVI*)

A mixture of 15.6 g of dimethoxy(2-methyl-1,4-pentadienyl)borane [(XV), b.p. 61–61.5° (18 mm), n_D^{20} 1.4418, d_4^{20} 0.8790[3]] and 60 ml of glacial acetic acid was heated for 6 h (98°). Distillation yielded 8.3 g (85%) of compound (XVI), b.p. 57.5–58.5° (750 mm), n_D^{20} 1.4067.

2,4-*Dinitrophenylhydrazone of* 2-*methyl*-4-*penten*-1-*al* (*XVII*)

2.5 ml of 30% H_2O_2 was added to a cooled mixture (−30°) of 0.68 g of dimethoxy(2-methyl-1,4-pentadienyl)borane (XV) and 90 ml of a solution of DNPH. The temperature of the mixture was gradually raised to 20°, the mixture being continuously shaken. After stirring for 2 h the precipitate was filtered and recrystallized from methanol. 9.4 g of 2,4-dinitrophenylhydrazone was obtained, m.p. 102–103°. (Found: C, 51.76; H, 5.00. $C_{12}H_{14}N_4O_4$ calcd.: C, 51.79; H, 5.07%.)

1-*Ethoxy*-1-*o*-*tolylethylene* (*XIX*)

To a solution of 9.8 g of tribenzylborane in 25 ml of THF at 0–5° was added 6.3 ml of ethoxyacetylene. The mixture became black and then (on stirring) became more clear. After stirring overnight the solvent was removed and to the residue 4.2 ml of ethanol was added, the temperature having raised simultaneously to 80°. The mixture was refluxed for 10 h; fractionation gave 9.1 g (78.6%) of (XIX), b.p. 81–82° (8 mm), n_d^{20} 1.5141. (Found: C, 81.40; H, 8.78. $C_{11}H_{14}O$ calcd.: C, 81.44: H, 8.69%.)

2,4-*Dinitrophenylhydrazone of o-methylacetophenone* (*XX*)

Reaction of 0.24 g of (XIX) and 35 ml of a solution of 2,4-DNPH yielded dinitrophenylhydrazone of *o*-methylacetophenone (XX), m.p. 167.5–168° (after having been chromatographed on alumina and recrystallized from methanol).

REFERENCES

1 B. M. Mikhailov and Yu. N. Bubnov, *Izv. Akad. Nauk SSSR, Ser. Khim.*, (1965) 1310
2 B. M. Mikhailov, Yu. N. Bubnov and S. I. Frolov, *Izv. Akad. Nauk SSSR, Ser. Khim.*, (1967) 2290.
3 S. I. Frolov, Yu. N. Bubnov and B. M. Mikhailov, *Izv. Akad. Nauk SSSR, Ser. Khim.*, (1969) 1996.
4 S. A. Korobeinikova, Yu. N. Bubnov and B. M. Mikhailov, *Izv. Akad. Nauk SSSR, Ser. Khim.*, (1969) 2212.
5 Yu. N. Bubnov, S. I. Frolov, V. G. Kiselev, V. S. Bogdanov and B. M. Mikhailov, *Zh. Obshch. Khim.*, 40 (1970) 1311.
6 Yu. N. Bubnov, S. I. Frolov, V. G. Kiselev and B. M. Mikhailov, *Zh. Obshch. Khim.*, 40 (1970) 1316.
7 B. M. Mikhailov, Yu. N. Bubnov, S. A. Korobeinikova and V. S. Bogdanov, *Zh. Obshch. Khim.*, 40 (1970) 1321.
8 B. M. Mikhailov, Yu, N. Bubnov, S. A. Korobeinikova and S. I. Frolov, *Izv. Akad. Nauk. SSSR, Ser. Khim.*, (1968) 1923.
9 B. M. Mikhailov, Yu. N. Bubnov and S. A. Korobeinikova, *Izv. Akad. Nauk. SSSR, Ser. Khim.*, (1969) 1631.

10 B. M. Mikhailov, Yu. N. Bubnov and S. A. Korobeinikova, *Izv. Akad. Nauk. SSSR, Ser. Khim.*, (1969) 2465.
11 Yu. N. Bubnov, S. I. Frolov, V. G. Kiselev, V. S. Bogdanov and B. M. Mikhailov, *Organometallics in Chemical Synthesis*, 1 (1970) 37.
12 Yu. N. Bubnov and B. M. Mikhailov, *Izv. Akad. Nauk SSSR, Ser. Khim.*, (1970) 2156.
13 B. M. Mikhailov, Yu. N. Bubnov and S. A. Korobeinikova, *Izv. Akad. Nauk SSSR, Ser. Khim.*, (1970) 2631.
14 Yu. N. Bubnov, S. A. Korobeinikova, G. V. Isaguljants and B. M. Mikhailov, *Izv. Akad. Nauk SSSR, Ser. Khim.*, (1970) 2023.
15 M. Laudemar, *Bull. Soc. Chim. Fr.*, (1962) 974.
16 R. Paul and S. Tchelitcheff, *Bull. Soc. Chim. Fr.*, (1953) 417.
17 M. Andrac, *Ann. Chim. (Paris)*, 9 (1964) 287–315.
18 M. F. Druesne, *C.R. Acad. Sci.*, 258 (1964) 6435.
19 A. T. Babayan, M. G. Indgikyan and L. P. Tumyanyan, *Dokl. Akad. Nauk Arm. SSR*, 36 (1965) 95.
20 F. Weiss, A. Lantz and A. Isard, *Bull. Soc. Chim. Fr.*, (1965) 3215.
21 D. E. Pearson and W. E. Cole, *J. Org. Chem.*, 20 (1955) 488.
22 L. N. Zakharkin and V. I. Stanko, *Izv. Akad. Nauk SSSR, Otd. Khim. Nauk*, (1960) 1896.
23 B. M. Mikhailov and A. Ja. Bezmenov, *Izv. Akad. Nauk SSSR, Ser. Khim.*, (1965) 931.
24 I. N. Nazarov, Zh. A. Krasnaya and V. P. Vinogradov, *Zh. Obshch. Khim.*, 28 (1958) 460.