Registry No.—3, 22931-96-0; **3** (3-d_1 derivative), 22931-97-1; **4**, 23031-06-3; **5**, 22931-98-2; **6**, 22931-99-3; **7**, 22932-00-9; **8**, 22932-01-0; **9**, 22932-13-4; **10**, 22932-14-5; **11**, 22932-15-6; **12**, 22932-16-7; **13**, 22932-02-1; **14**, 4564-84-5; **15**, 22932-03-2; **16**, 13733-16-9; **17**, 22932-05-4; **18**, 22932-06-5; **19**, 22932-07-6; 1,1-diphenyl-1,2-hexanediol, 22932-08-7; 1-phenyl-2-methyl-1,2-propanediol, 20907-13-5; 1-d_1-1-phenyl-2-methyl-1,2-propanediol, 22932-11-2; 1-d_1-1-phenyl-2-methyl-1,2-propanediol (1-benzoate), 22932-12-3.

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The Reaction of Grignard Reagents with α-Bromocrotonic and α-Bromocinnamic Acids

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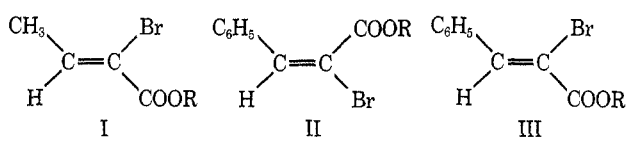
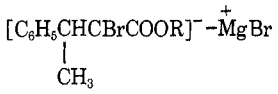
Phenylmagnesium bromide undergoes a 1,4 addition to α-bromocrotonic acid and its methyl ester. The α-bromoenolates formed are stable, and give on protonation two diastereoisomeric acids or esters. Methylmagnesium bromide reacts with *cis*- and *trans*-α-bromocinnamic acids and their esters in a 1,2 manner, but additional reactions were observed leading to other products such as 2-methylcinnamic acid.

The ratio of 1,4 to 1,2 addition of Grignard reagents to carbonyl compounds having a conjugated double bond depends on the functional group.[2,3] Introduction of a second functional group on the same carbon as the first, as in unsaturated malonates or cyanoacetates, enhances the 1,4 addition owing to a larger polarization of the double bond and a larger stabilization of the formed carbanion than in the monofunctional compounds. A bromine atom situated on a double bond directs electrophiles powerfully away from the carbon to which it is attached, but in nucleophilic additions the position of attack is less known. α-Bromo carbanions were obtained recently by transmetalation.[4] It was of interest therefore, to study the effect of an α-bromo substituent on the mode of addition to unsaturated acids.

Three acids and their methyl esters were studied, *trans*-2-bromocrotonic acid (I) and *cis*- (II) and *trans*-2-bromocinnamic acid (III). The first acid was treated



I II III



IV

a, R = H
b, R = CH_3

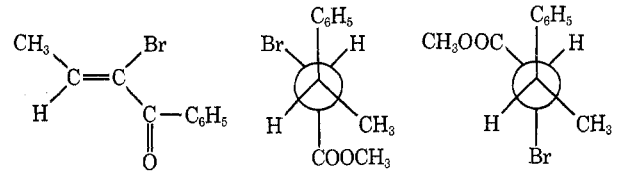
with phenylmagnesium bromide, and the other two with methylmagnesium bromide to test chemically whether the organanomagnesium derivatives formed by 1,4 addition are the same in all cases or depend on the starting materials.

All reactions were performed by two methods. In the first one ("preparative"), the products were isolated and characterized by their spectra and analyses. In the second ("analytical") method, smaller amounts of reagents and higher dilutions (sevenfold) than in the first were used and the products were analyzed by glpc only.

The reaction of Ia with phenylmagnesium bromide (3 or 5 equiv) gave similar results by both preparative and analytical methods. The addition was preferentially of the 1,4 type. *trans*-2-Bromocrotonophenone (V) was also formed by a 1,2 addition in about 10% yield. Two diastereoisomers, VI and VII, were obtained in a 2:1 ratio on protonation of the enolate. Their combined yield was approximately 70%. Addition of cuprous or cobaltous chloride to the Grignard reagent affected neither the amount of 1,4 addition nor the ratio of the diastereoisomers formed. Similarly, the 1,4 addition was the predominant mode of reaction of phenylmagnesium bromide with Ib. The ratio of diastereoisomers formed after treatment of the reaction mixture with water differed from that (1:1) from Ia. No influence of added cuprous or cobaltous chloride was found on the course of this reaction. No dilution effect was observed: the amount of 1,4 addition and the ratio of diastereoisomers were similar in the preparative and analytical reactions.

It is interesting that no carbene was formed from the enolate IV, even when its solution was left for several hours. Addition of cyclohexene did not yield a reaction product of a carbene, and the bromine atom was found in both products, that of the conjugate addition and that of the carbonyl addition.

The stereochemistry of *s-erythro*[5] VI and *s-threo* VII was tentatively assigned to the diastereoisomers on the



V VI′ VII′

(1) Taken from the M.S. Thesis of S. Z., The Hebrew University, 1967.
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TABLE I
NMR SPECTRA[a] OF THE DIASTEREOISOMERS VI AND VII

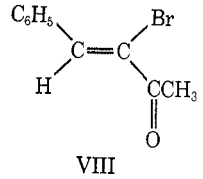
	C_6H_5	CH_3–C–H	BrCH	O–CH_3	C–CH_3	J_1,[b] cps	J_2,[c] cps
VI	7.25 (s, 5)	3.4 (m, 1)	4.27 (d, 1)	3.75 (s, 3)	1.33 (d, 3)	10	7
VII	7.24 (s, 5)	3.3 (m, 1)	4.27 (d, 1)	3.49 (s, 3)	1.47 (d, 3)	10	7

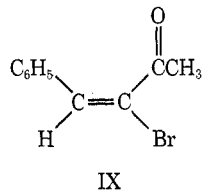
[a] Chemical shifts (δ, parts per million) of the protons from TMS as reference. In the parentheses are the multiplicity and number of protons by integration: s = singlet, d = doublet, m = multiplet. [b] J_1: coupling constant between the protons on CH and CHBr. [c] J_2: coupling constant between the protons on CH_3 and CH.

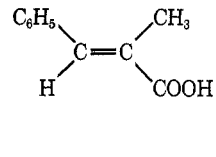
grounds of their nmr spectra (Table I). The coupling constant J_1 between the methine protons indicated[6] preference for the conformations VI′ and VII′ for the two isomers. This is reasonable, since all other possible conformations for the two diastereoisomers will have four vicinal *gauche* interactions of atoms or groups different from hydrogen. The two diastereoisomers differed significantly in the shifts of their methyl protons, CH_3O showing at a lower field in VI than in VII and CH_3–C appearing at a higher field in VI relative to VII. These differences were attributed to the diamagnetic shift of CH_3O in VII′ due to the presence of a phenyl group *gauche* to the ester and disposed at an angle which puts the methoxy group above the plane of the aromatic ring. Similar conformation of phenyl rings were found in 2-substituted arylcyclohexanes.[7] The downfield shift of CH_3–C in VII relative to VI is due to the presence in VII′ of a bromine atom *gauche* to this methyl group.

The stereochemistry of protonation of alicyclic enolates was studied and discussed by Zimmerman.[5] In the present case, the enolate of the ester yielded twice as much of the *erythro* VI as of the *threo* VII isomer, whereas equal amounts of the diastereoisomers were obtained from the acid Ia. These results are in agreement with the previsions based on the models of Zimmerman, which give more *erythro* from the ester than from the acid, since the first group is the larger.

The reaction of *cis*-α-bromocinnamic acid (IIa) with methylmagnesium bromide gave two principal products. One of them, obtained in a 20–30% yield, was a conjugated ketone, which differed from *trans*-α-bromobenzalacetone (VIII), but could be converted into VIII on treatment with acid, and was therefore its *cis* isomer


VIII


IX


X

IX. The other compound (10% yield in the analytical and 30% in the preparative method) was a conjugated acid not containing bromine, and analyzing for a methyl-substituted cinnamic acid. Ozonolysis of this compound gave benzaldehyde. The nmr spectrum of its methyl ester showed a phenyl at τ 7.24, one olefinic proton at 6.65, =C—CH_3 at 2.05, and –OCH_3 at 3.56. All these chemical shifts and the coupling constant[8,9] of 1.5 cps between the =C—CH_3 and the olefinic proton made it possible to assign to the acid the structure of *trans*-α-methylcinnamic acid X.

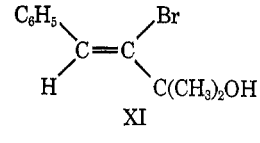
Similar products were obtained in the reaction of the ester IIb with methylmagnesium bromide. Products of condensation were also obtained in the preparative reactions of IIa and IIb. No conjugate addition to IIa of IIb was observed even in the presence of cuprous or cobaltous chloride.

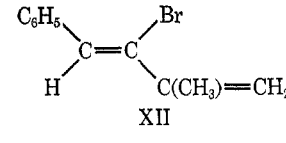
The formation of α-methylcinnamic acid (X) did not proceed through elimination of hydrogen bromide and subsequent addition of methylmagnesium bromide to phenylpropiolic acid, since the last acid reacted differently with this Grignard reagent.[10] The most likely explanation for the formation of X is a free radical reaction. Free radical processes were observed in many Grignard reactions.[11–13] Two mechanisms are conceivable. A methyl radical is added (1) to the double bond to give a stable benzylic radical, which then eliminates a bromine atom. A further mechanism (2), involving bromine atom abstraction, is also plausible. Reactions of this type were observed with organometallic compounds.[13]

$$C_6H_5CH{=}CBrCOOR + CH_3MgBr \longrightarrow C_6H_5\dot{C}HCBrCOOR{-}MgBr \longrightarrow C_6H_5CH{=}C(CH_3)COOR + MgBr_2 \quad (1)$$

$$C_6H_5CH{=}CBrCOOR + CH_3MgBr \longrightarrow C_6H_5CH{=}\dot{C}COOR \longrightarrow C_6H_5CH{=}C(CH_3)COOR \quad (2)$$

trans-α-Bromocinnamic acid (IIIa) gave, with methylmagnesium bromide, products of 1,2 addition only. The product of the reaction contained the conjugated *trans*-bromo ketone VIII (35–40%) (a 20% yield of this ketone was obtained by the preparative CuCl-catalyzed reaction) and the alcohol XI, which was identified by its infrared band at 3400 cm^{-1}. The last compound could not be separated and purified since it gave the


XI


XII

diene XII in a 30–40% yield on distillation and even during glpc analysis. In the same reaction, Kohler[14] obtained the alcohol XI only. In the uncatalyzed reaction with methylmagnesium bromide, the ester IIIb gave the ketone VIII (60% yield). No alcohol was obtained in the analytical reaction with ester IIIb, but XII was formed in the preparative reaction. Addition of cuprous or cobalt chloride did not change the course of the reaction, but the composition of the product changed in the preparative reactions of IIIa and IIIb. It seems that the catalyst facilitates a step subsequent to the first attack by methylmagnesium bromide and leading to condensation products. These were abundant in the products of the preparative catalyzed reactions. Very low amounts, if any, of α-methylcinnamic acid were obtained from IIIa or IIIb. It

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seems that the *cis* disposition of the phenyl and carboxyl groups in II hinders carbonyl addition more than in III, and at the same time facilitates either radical addition to the double bond (by relieving the *cis* interaction) or exposes the bromine atom to an atom transfer reaction (2).

The results show that an α-bromo substituent facilitates conjugate addition. Alkyl crotonates undergo 1,2 addition exclusively[15] unless the size of the alkyl group is large. Exclusive 1,4 addition in I is not a result of steric hindrance of the α substituent to 1,2 addition, since groups of similar size have a much weaker effect[12] on the ratio of 1,2 to 1,4 addition. The directive effect of the bromine is not strong enough to favor 1,4 over 1,2 addition in the α-bromocinnamic acids.

The absence of catalytic effect of added cuprous chloride on the proportion of conjugate addition indicates that methylcopper is not sufficiently reactive in the 1,4 addition to α-bromocinnamic acid to be able to compete with the 1,2 addition mode of methylmagnesium bromide. The same is true for α-bromocrotonic acid and ester. It seems that the α-bromo substituent hinders the usual 1,4 addition of methylcopper. This effect is difficult to understand on the basis of the mechanism recently proposed by House and Whitesides.[16] Methylcopper may possibly be inactivated by coordination with the bromine atom. However, halide salts are present in all Grignard reactions where 1,4 addition does occur, and 1,4 addition was observed in β-chloroacrylic acids.[17]

Experimental Section

All melting points and boiling points are uncorrected. Melting points were determined on the Thomas–Hoover apparatus.

The nmr spectra were run in carbon tetrachloride (unless otherwise stated) using TMS as an internal standard. The spectra were determined at 60 Mc on a Varian instrument, Model A-5660.

The infrared spectra were determined on a Perkin-Elmer instrument, Model 337, and the ultraviolet spectra on a Beckman uv spectrophotometer, Model DU, in ethanol solution.

trans-**2-Bromocrotonic acid (Ia)** was prepared by bromination of crotonic acid in dichloromethane and dehydrobromination of the product with pyridine:[18] mp 106°; $\bar{\nu}_{max}$ 3400, 1700, 1635 cm^{-1}; λ_{max} 228 mμ (ϵ 7000).

Esterification of this acid with diazomethane yielded methyl *trans*-2-bromocrotonate (Ib): bp 70° (10 mm); $\bar{\nu}_{max}$ 1725, 1625 cm^{-1}; λ_{max} 230 mμ (ϵ 4400). *Anal.* Calcd for $C_5H_7BrO_2$: C, 33.51; H, 3.91; Br, 44.69. Found: C, 33.55; H, 3.92; Br, 44.51.

cis-α-**Bromocinnamic acid (IIa)** was prepared by bromination of cinnamic acid in dichloromethane, dehydrobromination of the product with potassium hydroxide, and separation of the *cis* and *trans* acids in the form of their barium salts:[19] mp 120°; $\bar{\nu}_{max}$ 3400, 1700, 1625, 1580, 1500 cm^{-1}; λ_{max} 254 mμ (ϵ 12,000), 210 (14,000). Esterification of this acid with diazomethane yielded methyl-*cis*-α-bromocinnamate (IIb): $\bar{\nu}_{max}$ 1725, 1600, 1570, 1500 cm^{-1}; λ_{max} 250 mμ (ϵ 9600), 210 (12,000).[20] Distillation or glpc of the crude *cis* ester caused its isomerization to the *trans* form.

trans-α-**Bromocinnamic acid (IIIa)** was obtained[21] by addition of hydrogen bromide to phenylpropiolic acid:[22] mp 130°; $\bar{\nu}_{max}$ 3400, 1700, 1600, 1580, 1500 cm^{-1}; λ_{max} 273 mμ (ϵ 19,000), 217 (17,000). Treatment of this acid with diazomethane yielded methyl *trans*-α-bromocinnamate (IIIb): bp 132° (6 mm); $\bar{\nu}_{max}$ 1725, 1605, 1570, 1480 cm^{-1}; λ_{max} 292 mμ (ϵ 21,000), 220 (12,000).[20]

trans-**3-Bromo-4-phenylbut-3-en-2-one (VIII)** was prepared by bromination of benzalacetone and dehydrobromination with sodium acetate in ethanol:[23] bp 120° (1 mm); mp 30°; $\bar{\nu}_{max}$ 1680, 1600, 1575, 1490 cm^{-1}; λ_{max} 295 mμ (ϵ 18,000), 220 (11,000).

trans-**2-Bromo-1-phenylbut-2-en-1-one (V)** was obtained by bromination[24] of crotonophenone[25] and dehydrobromination with sodium acetate:[26] mp 68° (ethanol); $\bar{\nu}_{max}$ 1650, 1610, 1580 cm^{-1}; λ_{max} 252 mμ (ϵ 11,800).

This ketone was also prepared in a different way. *trans*-2-Bromocrotonic acid (16.5 g) and 30 ml of thionyl chloride were refluxed for 2 hr, then distilled, giving 15.5 g of the acid chloride boiling at 168°. This compound was added dropwise for 15 min to a mixture of 60 ml of benzene and 20 g of $AlCl_3$ cooled in an ice–water bath. The reaction mixture was poured on HCl and ice. The layers were then separated and the aqueous layer was washed twice with ether. Crystallization from ethanol gave 12 g of V.

Methyl 2-Bromo-3-phenylbutyrate (VIb and VIIb).—3-Phenylbutyric acid[27] (16.8 g) and 18 g of thionyl chloride were refluxed for 2 hr. A catalytic amount of red phosphorus was added, and then 16 g of bromine over 6 hr. The reaction mixture was poured into 75 ml of methanol, refluxed for 2 hr, and cooled. Water (100 ml) and ether (100 ml) were then added and the layers separated. The organic layer was washed with aqueous sodium bicarbonate, dried, and distilled, giving 18 g of product, bp 115° (1.5 mm). The product was a 1:1 mixture of two diastereoisomers. On cooling in a Dry Ice–methanol bath, this mixture precipitated a solid that crystallized in methanol, giving VI, mp 68°. *Anal.* Calcd for $C_{11}H_{13}BrO_2$: C, 51.36; H, 5.05; Br, 31.12. Found: C, 51.45; H, 5.00; Br, 30.98. The liquid remaining after precipitation of the solid contained the other diastereoisomer VII of 95% purity (glpc, nmr). *Anal.* Calcd for $C_{11}H_{13}BrO_2$: C, 51.36; H, 5.05; Br, 31.12. Found: C, 51.52; H, 5.06; Br, 30.92. For both isomers, the following spectral data were obtained: $\bar{\nu}_{max}$ 1740, 1600, 1500 cm^{-1}; λ_{max} 246 mμ (ϵ 2300), 213 (3500).

2-Bromo-1,3-diphenyl-butan-1-one.—Both diastereoisomers were obtained by bromination of 1,3-diphenylbutanone[28] and separation by fractional crystallization from hexane.[29] Diastereoisomer A: mp 80°; $\bar{\nu}_{max}$ 1675, 1590, 1575, 1480 cm^{-1}. Diastereoisomer B: mp 121°; $\bar{\nu}_{max}$ 1670, 1590, 1575, 1490 cm^{-1}.

TABLE II

NMR SPECTRA[a] OF THE PREPARED COMPOUNDS

Compound	Chemical shifts, δ,[b] of protons R_1	R_2	R	$J_{R_1R_2}$, cps
Ia	2.02 (d, 3)	7.60 (q, 1)		7
Ib	1.95 (d, 3)	7.36 (q, 1)	3.80 (s, 3)	7
IIa[c]	7.55 (s, 1)	7.35 (s, 5)		
IIb	8.25 (s, 1)	7.45 (m, 3) 7.91 (m, 2)	3.89 (s, 3)	
IIIa[c]	7.52 (m, 3) 7.96 (m, 2)	8.42 (s, 1)		
IIIb	7.46 (m, 3) 7.89 (m, 2)	8.22 (s, 1)	3.88 (s, 3)	
VIII	7.28 (m, 3) 7.75 (m, 2)	7.89 (s, 1)	2.43 (s, 3)	
V	2.03 (d, 3)	6.85 (q, 1)	7.61 (m, 5)	7

[a] In parentheses are the multiplicity and number of protons by integration: s = singlet; d = doublet; q = quartet; m = multiplet. [b] From tetramethylsilane (parts per million). [c] In $CDCl_3$.

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Grignard Reactions. A. Analytical Method.—Stock solutions of approximately 0.5 *F* methylmagnesium bromide and 0.5 *F* phenylmagnesium bromide were prepared and kept under nitrogen.

A solution of one mmol of the given acid in 25 ml of anhydrous ether was placed under nitrogen in a 50-ml flask provided with a rubber-capped neck. The solution was cooled in an ice–water bath, and 5 mmol of the Grignard reagent was added with a syringe. The solution was shaken intermittently. The work-up was different for the reaction of esters and of acids.

The reaction mixture of the Grignard reagent with the esters was left for 3 hr at room temperature, and poured on ice and hydrochloric acid. The layers were separated, and the organic layer was washed with aqueous sodium bicarbonate and then with water. The solution was dried on $MgSO_4$, the ether evaporated, and the residue dissolved in a known amount of dichloromethane and analyzed by glpc.

The reaction of the Grignard reagent with the acids proceeded for 6 hr. The mixture was poured on ice and hydrochloric acid. The organic layer was washed twice with 25 ml of 10% aqueous sodium carbonate, then with water. The neutral organic layer was analyzed as in the case of the esters. The alkaline layer was acidified, extracted with ether, and esterified with diazomethane. Evaporation of the ether left a residue, which was dissolved in dichloromethane and analyzed by glpc.

Ten milligrams of cuprous chloride or cobaltous chloride was added, in the catalyzed reactions, to the substrate before the addition of the Grignard reagent.

B. Preparative Method.—The Grignard reagent was prepared under nitrogen in a three-necked flask equipped with a condenser, dropping funnel, and mechanical stirrer, from 3.6 g (0.15 g-atom) of magnesium, 23.5 g of bromobenzene, and 200 ml of ether. The required amount of methyl bromide replaced bromobenzene in the case of methylmagnesium bromide. Cuprous chloride (250 mg) was added to the Grignard reagent in catalyzed reactions before the addition of the substrate.

Reaction with Esters.—A solution of 0.05 mol of the ester in 100 ml of ether was added dropwise to the Grignard reagent, under nitrogen, with stirring and cooling in an ice bath. The solution was stirred for 3 hr and poured onto ice and hydrochloric acid. The organic layer was washed with sodium bicarbonate solution and distilled.

Reaction with Acids.—The acid (0.05 mol) was added as above, but the reaction mixture was stirred for 6 hr and then poured onto ice and hydrochloric acid. The acid and neutral products were separated as in the analytical method, and distilled after conversion of the acids into esters.

2-Bromo-1-phenyl-3-methyl-1,3-butadiene (XII) was obtained in the reaction of methylmagnesium bromide with *trans*-α-bromocinnamic acid: bp 98–104° (0.8 mm); $\bar{\nu}_{max}$ 900 cm^{-1}; λ_{max} 275 mμ (ε 17,000). *Anal.* Calcd for $C_{11}H_{11}Br$: C, 59.19; H, 4.93; Br, 35.87. Found: C, 59.03; H, 4.92; Br, 35.97.

Methyl *trans*-α-methylcinnamate was obtained after the esterification of the acid product of the reaction of *cis*-α-bromocinnamic acid with methylmagnesium bromide: $\bar{\nu}_{max}$ 1725, 1630, 1600, 1580, 1500 cm^{-1}; λ_{max} 256 mμ ((ε 10,000), 210 (13,000); nmr (CCl_4) δ 7.24 (C_6H_5), 6.65 (d, =CH), 2.05 (d, =C—CH_3), 3.56 (s, —OCH_3). Hydrolysis and crystallization from hexane gave the free acid, mp 75°.[30,31]

1-Phenyl-3-methylbut-1-yn-3-ol was obtained in an attempt to prepare the alcohol XI. A solution of 11 g of VIII in 100 ml of ether was added dropwise with cooling and stirring under nitrogen to a solution of methyllithium, prepared from 1.4 g of lithium and methyl bromide in 200 ml of ether. The reaction mixture was stirred for 20 min, then poured onto ice and hydrochloric acid. The organic layer was distilled and gave 4 g: bp 84–90° (0.6 mm); mp 50°;[32] $\bar{\nu}_{max}$ 3330, 2200, 1600, 1575, 1480 cm^{-1}; λ_{max} 252 mμ (ε 21,000), 240 (24,000); nmr (CCl_4) 7.55 (m, $-C_6H_5$), 1.77 (s, —CH_3), 3.11 (OH).

Gas Chromatography Study.—Analyses of the products obtained in the analytical and preparative methods were performed by glpc on a 1.5 m × 0.25 ft column of 10% stabilized polydiethylene glycol succinate on Chromosorb P or on 20% SE-30 on Chromosorb P at 160–220°, depending on the compounds. Solutions of the reaction products in dichloromethane containing a known amount of an internal standard (benzophene) were injected.

The yields in the preparative method estimated by glpc differed by not more than 5–8% from those of products actually isolated.

Registry No.—Ia, 5405-34-5; Ib, 22966-48-9; IIa, 15894-30-1; IIb, 21788-35-2; IIIa, 15813-24-8; IIIb, 21788-36-3; V, 22965-93-1; VIb, 22965-94-2; VIIb, 22965-95-3; VIII, 22965-96-4; XII, 22965-97-5; 2-bromo-1,3-diphenylbutan-1-one, 7472-59-5; methyl *trans*-α-methylcinnamate, 22946-43-6; 1-phenyl-3-methylbut-1-yn-3-ol, 1719-19-3.

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