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Reactions with α-Diazo Ketones. III.[1] The Stereochemical Course of Cyclization of Some Olefin-Substituted α-Diazo Ketones

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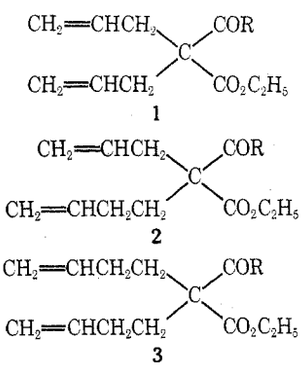
Catalytic decomposition of the suitably substituted ethyl diazoacetoacetates **1b**, **2b**, and **3b** yielded 3-allyl-3-carbethoxybicyclo[3.1.0]hexan-2-one (**4**), 3-(but-3-enyl)-3-carbethoxybicyclo[3.1.0]hexan-2-one (**11**), and 3-(but-3-enyl)-3-carbethoxybicyclo[4.1.0]heptan-2-one (**12**), respectively, all three formed by intramolecular addition of the intermediate ketocarbenoid species to the olefinic bond present in the molecules. The keto esters **4** and **11** were further reduced with $NaBH_4$ and $LiAlH_4$ to the corresponding ester alcohols and diols, respectively. Steric assignment of both the keto esters and the alcohols was based on investigation of their nmr spectra and comparison with spectral data obtained for the simpler model compounds **9a**, **9b**, **10a**, and **10b**, synthesized from 2-carbethoxycyclopentanone. The ring closure of the diazo ketones to the bicyclo[3.1.0]hexan-2-ones seems to be stereoselective, giving preferentially the isomer in which the cyclopropane ring and the carbethoxy group are located trans to each other.

In connection with a project of intramolecular cyclization of bisdiazo ketones,[1,2] it was necessary to investigate the stereochemical course of the ring closure of some related monodiazo compounds.

We wish to report now our results obtained from catalytic decomposition of the monodiazo ketones **1b**, **2b**, and **3b**, prepared by standard procedures from the diesters **1a**, **2a**, and **3a**. The crude diazo compounds, contaminated with chloro ketones, were not purified, but directly decomposed with catalytic amounts of π-allylic palladium chloride complex.[2,3]



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2

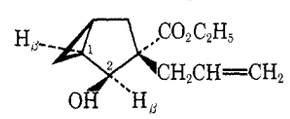
3

a, R = OC_2H_5
b, R = CHN_2

Decomposition of the diallyl compound **1b** gave the 3-allyl-3-carbethoxybicyclo[3.1.0]hexan-2-one (**4**) as the major product.

The configurational assignment of **4** is based on nmr data obtained for compound **4** itself and for the alcohols **5** and **6**. As we showed earlier[2] in detail, the resonance of the geminal cyclopropyl protons is a good indicator of the steric relationship between the cyclopropane ring and a carbonyl group attached at C_3 in the bicyclo[3.1.0]hexane system. In accordance, the presence of the one-proton upfield multiplet centered at δ 0.98 ppm in the spectrum of **4**, due to the endo proton $H_{6\alpha}$, indicates that this proton is anisotropically unaffected by the ester carbonyl group. Thus, the cyclopropane and the carbethoxy group should be trans located to each other.

In order to obtain further spectral evidence, small samples of **4** were reduced with $NaBH_4$ and $LiAlH_4$ to the hydroxy ester **5** and the diol **6**, respectively, and their nmr



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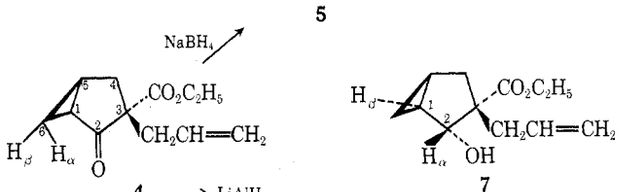
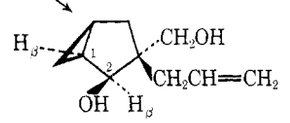


4 **7**

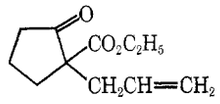


6

spectra were investigated. The most significant feature of the spectra was the presence of a doublet attributed to the tertiary proton $H_{2\beta}$ and observed at δ 4.82 and 4.41 ppm for compounds **5** and **6**, respectively. The splitting of these absorptions to a doublet is reasonably explained as resulting from coupling with the cis proton $H_{1\beta}$;[4] *e.g.*, the C_2 hydroxyl and the cyclopropane ring have to be cis related to each other.[6] It is important to note the large difference (Δ = 4.80 − 4.40 = 0.40 ppm) in the chemical shifts observed for the $H_{2\beta}$ in the spectra of alcohols **5** and **6**. This difference is apparently induced by the anisotropy of the carbonyl group[9] present only in the hydroxy ester **5** and clearly indicates the cis relationship between this proton and the carbethoxy group in this compound.

The reliability of this method in stereochemical investigations of suitably substituted cyclopentane ring systems could be demonstrated on the stereoisomeric model com-

pounds **9** and **10**, obtained by reduction of the parent keto ester **8**, and also by interconversion (**9a** → **9b** and **10a** → **10b**) (see Experimental Section). The difference in the chemical shifts of the tertiary proton H′ calculated from the spectral data of **10a** and **10b** has been found significantly larger (Δ = 0.30 ppm) than the corresponding difference (Δ = 0.10 ppm) calculated from the spectra of **9a** and **9b** (details in Experimental Section). This finding would predict a cis relationship between H′ and the R group in **10a** and **10b**. The classical method of acetonide formation from **9b** but not from **10b** verified the above prediction.



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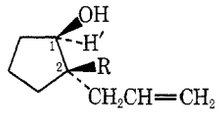
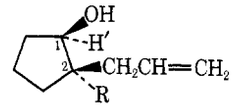
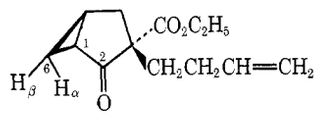


9a, R = $CO_2C_2H_5$
b, R = CH_2OH

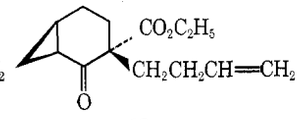


10a, R = $CO_2C_2H_5$
b, R = CH_2OH

Decomposition of the unsymmetrical diazo ketone **2** to the keto ester **11** clearly showed the preferential ketocarbenoid cyclization to the bicyclohexanone *vs.* the alternative bicycloheptanone ring system.[10] Steric assignment of compound **11** was based on the nmr spectrum, found very similar to that of keto ester **4** and revealing the important $H_{6\alpha}$ resonance at δ 0.9 ppm (center of multiplet). Further support was obtained after $NaBH_4$ reduction and spectral investigation of the resulting alcohol (see Experimental Section).



11



12

Cyclization of the homologous dibut-3-enyl diazo ketone **3** to the keto ester **12** occurred only in 25% yield, demonstrating again the more difficult formation of the bicycloheptanone system (*vide supra*). Although spectral data of this compound were insufficient to provide clear-cut evidence for the stereochemistry, by analogy to the previous cases a relative trans relationship between the cyclopropane ring and the carbethoxy group is suggested.

Experimental Section[11]

Materials. Diethyl diallylmalonate (**1a**) was commercially available. Diethyl allyl(but-3-enyl)malonate (**2a**) was prepared as previously described.[1]

Diethyl Dibut-3-enylmalonate (3a). Diethyl malonate (32 g, 0.2 mol) was added dropwise with stirring to a suspension of sodium hydride (4.8 g, 0.2 mol) in dry dimethylformamide (100 ml). Stirring was continued until all the hydride had reacted and to the mixture 4-bromobut-1-ene (27 g, 0.2 mol) was added dropwise. The reaction was exothermic. After addition was completed the solution was stirred for 0.5 hr at room temperature; then sodium hydride (4.8 g, 0.2 mol) was added again in portions, followed by 4-bromobut-1-ene (27 g, 0.2 mol).[12] After stirring at 80° for 2 hr, the reaction mixture was poured into cold water and extracted with ether. The ether solution was washed with water and dried over Na_2SO_4 and the solvent was removed. Distillation of the oily residue gave 40 g (75%) of the desired ester: bp 139–141° (10 mm); ir ($CHCl_3$) 1730 (ester C=O), 1645 cm^{-1} (CH_2=CH-).

Anal. Calcd for $C_{15}H_{24}O_4$: C, 67.13; H, 9.02. Found: C, 67.46; H, 9.08.

Preparation of the Diazo Ketones 1b, 2b, and 3b. A cooled solution of solid KOH (0.13 mol) in anhydrous ethanol (100 ml) was added to the corresponding diester **1a**, **2a**, or **3a**, (0.1 mol) in anhydrous ethanol (100 ml) and the mixture was kept at room temperature overnight. The ethanol was then removed (water pump), water was added, and the cooled solution was washed twice with ether. From the dried ether solution the unreacted diesters could be regenerated. The aqueous layer was acidified with cold 10% HCl and extracted several times with ether. From the combined, dried (Na_2SO_4) ethereal extracts the oily monoacids were isolated in 70–75% yield. Their nmr spectra exhibited signals for one $-CH_2CH_3$ group and one -COOH (δ 9.5–10.00 ppm); the latter disappeared on addition of D_2O.

To a magnetically stirred and ice-cooled mixture of the corresponding monoacid (0.1 mol), dry benzene (100 ml), and anhydrous pyridine (1 ml), a solution of freshly distilled oxalyl chloride (30 ml) in dry benzene (50 ml) was added dropwise. After the addition was completed the ice bath was removed and the mixture was slowly heated to 40° and kept at this temperature for 2 hr and then at 60° for an additional 2 hr. Excess oxalyl chloride and benzene were removed and the residue was washed three times with dry ether. The combined ethereal extracts on evaporation gave the crude acid chloride: ir (CCl_4) 1800 (-COCl), 1745–1750 ($-CO_2C_2H_5$), 1645 cm^{-1} (CH_2=CH-).

A solution of the crude acide chloride (0.1 mol) in dry ether (*ca.* 400 ml) was added dropwise under swirling to an ice-cold ethereal diazomethane solution [prepared from nitrosomethylurea (65 g) with 40% KOH solution (200 ml) in ether (650 ml)]. After standing for 1 hr, the solution was filtered and the solvent was removed under reduced pressure to give the crude, oily diazo ketone **1b**, **2b**, or **3b**. The diazo ketones had the characteristic ir absorption at 2110 cm^{-1} and in the nmr spectrum the resonance for the diazo ketone proton ($-COCHN_2$) was observed at δ 5.50, 5.52, and 5.62 ppm for **1b**, **2b**, and **3b**, respectively.

3-Allyl-3-carbethoxybicyclo[3.1.0]hexan-2-one (4). A cold solution of crude, freshly prepared diazo ketone **1b** (10 g, 42 mmol) in dry ether (500 ml) was added dropwise to a magnetically stirred ice-cold suspension of π-allylic $PdCl_2$ complex (0.1 g, 0.38 mmol) in dry ether (200 ml). After the addition was completed, stirring was continued without cooling until the ir band at 2110 cm^{-1} disappeared. After filtration and concentration of the solution the residue (*ca.* 8.5 g) was distilled and the fraction boiling at 70–80° (0.3 mm) was collected (6.1 g). Purification by preparative vpc on a 6 ft × 0.375 in. column of 3% XE-60 on 60-80 mesh Chromosorb W at 150° followed by redistillation at 75° (0.2 mm) gave the keto ester **4**: ir ($CHCl_3$) 1720 (ketone C=O), 1740 (ester C=O), 1640 cm^{-1} (CH_2=CH-); nmr δ 0.98 (m, 1 H, H_α), 1.27 (t, 3 H, $-CH_2CH_3$), 4.88–6.10 ppm (m, 3 H, CH_2=CH-); mass spectrum *m/e* 208 (M^+).

Anal. Calcd for $C_{12}H_{16}O_3$: C, 69.21; H, 7.74. Found: C, 69.30; H, 7.92.

For spectroscopic investigation small samples (0.1–0.2 g) of **4** were reduced with $NaBH_4$ and $LiAlH_4$ by using standard procedures. Data recorded for the $NaBH_4$-reduction product (suggested structure **5**): ir ($CHCl_3$) 3590, 1720, 1640 cm^{-1}; nmr δ 0.55 (m, 2 H, $H_{6\alpha}$, $H_{6\beta}$), 1.25 (t, 3 H, $-CH_2CH_3$), 4.15 (q, 2 H, $-CH_2CH_3$), 4.81 (d, 1 H, $H_{2\beta}$, J = 5.5 Hz), 4.90–6.05 ppm (m, 3 H, CH_2=CH-); mass spectrum *m/e* 210 (M^+). Data recorded for $LiAlH_4$-reduction product (suggested structure **6**): ir ($CHCl_3$) 3600, 3450, 1645 cm^{-1}; nmr δ 0.56 (m, 2 H, $H_{6\alpha}$, $H_{6\beta}$), 3.24 and 3.38 for δ_B and δ_A of AB (2 H, $-CH_2OH$, J_{AB} = 11 Hz), 4.41 (d, 1 H, $H_{2\beta}$, J = 6 Hz), 4.90–6.10 ppm (m, 3 H, CH_2=CH-); mass spectrum *m/e* 150 ($M^+ - H_2O$).

2-Allyl-2-carbethoxycyclopentanone (8). This was prepared by alkylation of 2-carbethoxycyclopentanone (31.2 g, 0.2 mol) with allyl bromide (25 g, 0.2 mol) and sodium hydride (4.8 g, 0.2 mol) in dry DMF (*ca.* 100 ml) by the method described for the preparation of **3**. The pure keto ester was obtained in 72% yield and had bp 133° (16 mm) [lit.[13] bp 131° (14 mm)].

Reduction of 8 with $NaBH_4$. To a magnetically stirred solution of **8** (4 g, 20.4 mmol) in methanol (100 ml), $NaBH_4$ (1 g, 26.5 mmol) was added in portions. The mixture was left overnight at room temperature, the solvent was removed, and water was added. The solution was then neutralized (pH 7) with dilute HCl and extracted with ether. After the usual work-up 3.6 g (89%) of an oily product was isolated, bp 100° (25 mm). Vpc analysis of this oil (3% XE-60 on Gas-Chrom Q) showed the presence of two major peaks in the ratio of 40:60 corresponding to the isomeric cyclopentanols **9a** and **10a**, respectively. They were separated by preparative vpc on a 5 ft × 0.375 in. column of 15% XE-60 on Chromosorb W at 150°, gas flow rate 100 ml/min.

(1*RS*,2*RS*)-2-Allyl-2-carbethoxycyclopentan-1-ol (9a) was a liquid: retention time 17 min; ir ($CHCl_3$) 3490–3580 (broad), 1710,

1730, 1645 cm^{-1}; nmr δ 1.27 (t, 3 H, $-CH_2CH_3$), 4.10 (m, 1 H, H′, partly overlapped by the quartet due to $-CH_2CH_3$), 4.20 (q, 2 H, $-CH_2CH_3$), 4.80–6.20 ppm (m, 3 H, CH_2=CH–).

Anal. Calcd for $C_{11}H_{18}O_3$: C, 66.64; H, 9.15. Found: C, 66.72; H, 9.10.

(1*RS*,2*SR*)-2-Allyl-2-carbethoxycyclopentan-1-ol (10a) was a liquid: retention time 24 min; ir 3590, 1720, 1645 cm^{-1}; nmr δ 1.25 (t, 3 H, $-CH_2CH_3$), 4.16 (q, 2 H, $-CH_2CH_3$), 4.39 (m, 1 H, H′, partly overlapped by the quartet due to $-CH_2CH_3$), 4.80–6.20 ppm (m, 3 H, CH_2=CH–).

Anal. Calcd for $C_{11}H_{18}O_3$: C, 66.64; H, 9.15. Found: C, 66.70; H, 9.08.

Reduction of 8 with $LiAlH_4$. Preparation of (1*RS*,2*SR*)-2-Allyl-2-hydroxymethylcyclopentan-1-ol (9b) and (1*RS*,2*RS*)-2-Allyl-2-hydroxymethylcyclopentan-1-ol (10b). To a magnetically stirred ethereal slurry (50 ml) of $LiAlH_4$ (1.7 g, 45 mmol) the solution of **8** (3.4 g, 17.3 mmol) in dry ether (50 ml) was added dropwise. The mixture was stirred at room temperature overnight, excess $LiAlH_4$ was destroyed by cautious addition of ethyl acetate, and the solvent was removed. The crude oily residue (2.1 g) was dissolved in dry acetone (100 ml), 70% aqueous perchloric acid (0.5 ml) was added, and the mixture was kept at room temperature for 1 hr. Neutralization with solid Na_2CO_3, filtration, and removal of the solvent left a mixture which was separated by chromatography on Florisil (60–100 mesh, 50 g). Elution with petroleum ether (bp 40–60°), followed by short-path distillation [80° (bath temperature) at 25 mm] gave 0.25 g (7.4%) of the oily acetonide of diol **9b**: ir ($CHCl_3$) 1630 (CH_2=CH–), 1375, 1365 cm^{-1} [$(CH_3)_2C$=]; nmr δ 1.37 (two s, 6 H), 3.82 (badly resolved t, 1 H), AB quartet at 3.45 and 3.68 ppm (2 H, J_{AB} = 12 Hz).

Anal. Calcd for $C_{12}H_{20}O_2$: C, 73.43; H, 10.27. Found: C, 73.37; H, 10.20.

Elution with $CHCl_3$ gave 1.7 g (63%) of **10b**, which was recrystallized from cyclohexane: mp 56°; ir ($CHCl_3$) 3620, 3560, 1645 cm^{-1}; nmr δ 3.33 and 3.60 (AB quartet, 2 H, $-CH_2OH$, J_{AB} = 11 Hz), 4.09 (t, 1 H, H′), 4.80–6.20 ppm (m, 3 H, CH_2=CH–).

Anal. Calcd for $C_9H_{16}O_2$: C, 69.19; H, 10.32. Found: C, 69.40; H, 10.09.

The above-described acetonide was hydrolyzed in ether solution with a few drops of hydrochloric acid. After the usual work-up the crude oily diol was purified by chromatography on Florisil (elution with chloroform) and short-path distilled [85° (bath temperature) at 0.1 mm] to give **9b**: ir ($CHCl_3$) 3580, 3420, 1645 cm^{-1}; nmr δ 3.60 and 3.70 (AB quartet, 2 H, $-CH_2OH$, J_{AB} = 10 Hz), 4.00 ppm (t with fine splitting, 1 H, H′).

Anal. Calcd for $C_9H_{16}O_2$: C, 69.19; H, 10.32. Found: C, 69.50; H, 10.42.

Conversion of 9a to 9b. To a dry ethereal solution (50 ml) of the hydroxy ester **9a** (0.1 g, 0.5 mmol), $LiAlH_4$ (0.05 g, 1.3 mmol) was added and the mixture was stirred for 0.5 hr. Excess reagent was decomposed with ethyl acetate and after the usual work-up the oily product was identified as the cis diol **9b** by ir, nmr, and mass spectrum. The product gave an acetonide derivative identical with that described above.

Conversion of 10a to 10b. The hydroxy ester **10a** (0.1 g, 0.5 mmol) in dry ether (50 ml) was treated with $LiAlH_4$ (0.05 g, 1.3 mmol) as described for the reduction of **9a**. The solid product was found to be identical with the trans diol **10b** in melting point, mixture melting point, and spectral properties.

3-(But-3-enyl)-3-carbethoxybicyclo[3.1.0]hexan-2-one (11). The crude, freshly prepared diazo ketone **2b** (6.5 g, 26 mmol) in dry ether (200 ml) was added dropwise to a magnetically stirred, ice-cold suspension of π-allylic $PdCl_2$ complex (0.09 g, 0.35 mmol) in dry ether (500 ml). After addition was completed, stirring was continued overnight at room temperature. After filtration and concentration of the solution, the residue (*ca.* 4.8 g) was distilled [70–85° (0.2 mm)], then purified by preparative vpc on a 6 ft × 0.375 in. column of 3% XE-60 on 60–80 mesh Chromosorb W at 140°. The major peak was collected and short-path distilled twice [70° (0.2 mm)] to give **11** as an oil: ir ($CHCl_3$) 1720 (ketone C=O), 1745 (ester C=O), 1645 cm^{-1} (CH_2=CH–); nmr δ 0.90 (m, 1 H, $H_{6\alpha}$), 1.27 (m overlapped by a t, 4 H, $H_{6\alpha}$ and $-CH_2CH_3$), 4.20 (q, 2 H, $-CH_2CH_3$), 4.80–6.20 ppm (m, 3 H, CH_2=CH–); mass spectrum *m/e* 222 (M^-).

Anal. Calcd for $C_{13}H_{18}O_3$: C, 70.24; H, 8.16. Found: C, 70.12; H, 8.20.

Reduction of 11 with $NaBH_4$. The keto ester **11** (0.7 g, 3.2 mmol) was reduced with $NaBH_4$ (0.25 g, 6.6 mmol) in methanol (20 ml) and after the usual work-up 0.5 g (71%) of crude product was obtained and purified by short-path distillation at 110° (25 mm) to give **3-(but-3-enyl)-3-carbethoxybicyclo[3.1.0]hexan-2-ol**: nmr δ 0.62 (m, 2 H, $H_{6\alpha}$, $H_{6\beta}$), 1.25 (t, 3 H, $-CH_2CH_3$), 4.17 (q, 2 H, $-CH_2CH_3$), 4.78 (d, 1 H, $H_{2\beta}$), 4.80–6.20 ppm (m, 3 H, CH_2=CH–).

Anal. Calcd for $C_{13}H_{20}O_3$: C, 69.61; H, 8.99. Found: C, 69.50; H, 8.79.

After reduction of a sample of **11** with $LiAlH_4$ the resonance due to $H_{2\beta}$ shifted to higher field and resonated at δ 4.33 ppm.

3-(But-3-enyl)-3-carbethoxybicyclo[4.1.0]heptan-2-one (12). Freshly prepared, crude diazo ketone **3b** was decomposed under the same condition as described for the decomposition of **2b**. A preliminary high-vacuum distillation of the crude reaction mixture separated volatile products from polymeric materials. The volatile fraction was then redistilled through a short Vigreux column and the main fraction [bp 90–105° (0.15 mm)] was collected. Further purification by preparative vpc (3% SE-30 on Chromosorb W) gave the keto ester **12** in 25% yield: ir ($CHCl_3$) 1730, 1690 cm^{-1}; nmr δ 0.80–1.40 (m, 2 H, $H_{6\alpha}$, $H_{6\beta}$), 1.24 (t, 3 H, $-CH_2CH_3$), 4.20 (q, 2 H, $-CH_2CH_3$), 4.80–6.20 ppm (m, 3 H, CH_2=CH–); mass spectrum *m/e* 236 (M^+).

Anal. Calcd for $C_{14}H_{20}O_3$: C, 71.16; H, 8.53. Found: C, 72.46; H, 8.68.

Registry No.—**1a**, 3195-24-2; **1b**, 51481-45-9; **2a**, 51481-46-0; **2b**, 51481-47-1; **3a**, 51481-48-2; **3b**, 51540-13-7; **4**, 51481-49-3; **5**, 51481-50-6; **6**, 51481-51-7; **8**, 41975-67-1; **9a**, 51481-52-8; **9b**, 51481-53-9; **9b** acetonide, 51481-54-0; **10a**, 51481-55-1; **10b**, 51540-12-6; **11**, 51481-56-2; **12**, 51481-57-3; diethyl malonate, 105-53-3; 4-bromobut-1-ene, 5162-44-7; 2-carbethoxycyclopentanone, 611-10-9; allyl bromide, 106-95-6; 3-(but-3-enyl)-3-carbethoxybicyclo[3.1.0]hexan-2-ol, 51481-58-4.

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(2) S. Bien and D. Ovadia, *J. Org. Chem.*, **35**, 1028 (1970).
(3) R. K. Armstrong, *J. Org. Chem.*, **31**, 618 (1966).
(4) In the isomeric hydroxy ester **7** with an $H_{2\alpha}$ configuration the relevant dihedral angle ($H_{2\alpha}$–C–C–$H_{1\beta}$) would be approximately 90° and therefore no spin–spin coupling should be observed.[2,5]
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(9) The inductive effect would be practically negligeable through four bonds.
(10) M. M. Fauzi and C. D. Gutsche, *J. Org. Chem.*, **31**, 1390 (1966).
(11) Melting points were taken in capillaries and are uncorrected. The ir spectra were determined on a Perkin-Elmer Infracord spectrophotometer. Nmr spectra were recorded on a Varian T-60 or on a Varian A-60 spectrometer in $CDCl_3$ solution using TMS as internal standard. Vpc analyses were done on a Varian Aerograph Model 90-P gas chromatograph.
(12) The sodium hydride was allowed to react completely before addition of the bromide was started.
(13) H. Christol, M. Mousseron, and F. Plenat, *Bull. Soc. Chim. Fr.*, 543 (1959).