Tetra-1(*E*)-propenyldistibine (18). Compound **18** was prepared by method b from 4.0 g (16 mmol) of tri-1(*E*)-propenylstibine and 0.74 g (32 mmol) of sodium in 100 mL of liquid ammonia. A 77% yield (2.5 g) of pure **18** was obtained as a yellow, air-sensitive liquid which freezes, mp −4 to −3 °C, to a yellow solid: ^{1}H NMR (C_6D_6) δ 1.80 (apparent d, 12 H), 6.15 (m, 8 H); IR (CCl_4) 2990 (m), 2962 (m), 2942 (m), 2915 (s), 2870 (w), 2850 (m), 1609 (s), 1443 (s), 1375 (w), 1320 (w), 1200 (w) cm^{-1}; UV–visible (cyclohexane) λ_{max} <220 nm. Anal. Calcd for $C_{12}H_{20}Sb_2$: C, 35.34; H, 4.94. Found: C, 35.43; H, 4.78.

Tetra-2(*E*)-but-2-enyldistibine (21). Method d. Potassium metal (0.63 g, 16 mmol) in pieces was added to 2.3 g (8.0 mmol) of tri-2(*E*)-but-2-enylstibine in 100 mL of liquid ammonia. After the deep red solution was allowed to stir for 1 h, 0.78 g of ammonium bromide was added. After 30 min, 0.34 mL of 1,2-dibromoethane was added dropwise. The ammonia was allowed to evaporate and 50 mL of pentane was added. The solution was filtered, and the pentane was evaporated under reduced pressure. Four recrystallizations from cold pentane gave 1.28 g (69%) of pure **21** as a yellow, air-sensitive liquid which freezes, mp 2.5–3.5 °C, to a yellow solid: ^{1}H NMR (C_6D_6) δ 1.58 (m, 12 H), 2.12 (m, 12 H), 6.00 (m, 4 H); IR (CCl_4) 3006 (m), 2936 (m), 2917 (m), 2855 (m), 1614 (w), 1436 (m), 1374 (w) cm^{-1}; UV–visible (cyclohexane) λ_{max} 280 nm (ϵ 12400); diffuse reflectance, maximum absorbance 350 nm. Anal. Calcd for $C_{16}H_{28}Sb_2$: C, 41.43; H, 6.08. Found: C, 41.28; H, 6.06.

Tetrakis(2-methyl-1-propenyl)distibine (20). Method e. Antimony trichloride (1.19 g, 5.2 mmol) and 3.0 g (10.5 mmol) of tris(2-methyl-1-propenyl)stibine in 15 mL of tetrahydrofuran were stirred for 30 min. Distillation of the residue at reduced pressure gave 3.7 g (88%) of bis(2-methyl-1-propenyl)antimony chloride as an air-sensitive liquid which decomposed on standing: bp 69–70 °C (0.08 torr); ^{1}H NMR (C_6D_6) δ 1.65 (apparent d, 18 H), 6.50 (m, 3 H); MS, *m/e* (relative intensity) 267 (1.0, M$^+$), 265 (0.6), 233 (0.9), 231 (1.3), 178 (13.8), 176 (19.3), 123 (8.7), 121 (12.8), 110 (83.0), 95 (54.3), 55 (100).

Tetrakis(2-methyl-1-propenyl)distibine was prepared from 2.2 g (8.3 mmol) of bis(2-methyl-1-propenyl)antimony chloride and 0.38 g (16.5 mmol) of sodium in 100 mL of liquid ammonia. The yield was 1.55 g (81%). Alternatively, **20** could be prepared in 76% yield by method d. Compound **20** may be purified by recrystallization from pentane at −20 °C. It is a yellow air-sensitive solid which melts, mp 49–51 °C, to a yellow liquid: ^{1}H NMR (C_6D_6) δ 1.90 (s, 24 H), 6.40 (br s, 4 H); IR (CCl_4) 2960 (m), 2930 (m), 2904 (s), 2850 (w), 1608 (m), 1440 (s), 1380 (w), 1370 (w), 1278 (w) cm^{-1}; UV–visible (cyclohexane) 312 (ϵ 1630), 294 (1630), 207 nm (22700); diffuse reflectance, maximum absorbance 290 nm. Anal. Calcd for $C_{16}H_{28}Sb_2$: C, 41.43; H, 6.08. Found: C, 41.50; H, 6.02.

Acknowledgment. Support of our work by the A.F. O.S.R. (Grant No. 81-099) is gratefully acknowledged.

Registry No. **16**, 87011-60-7; **17**, 86993-83-1; **18**, 86993-85-3; **19**, 86993-84-2; **20**, 86993-87-5; **21**, 86993-86-4; **22** (R = vinyl), 5613-68-3; **22** (R = isopropenyl), 87011-57-2; **22** (R = 1(*Z*)-propenyl), 86993-81-9; **22** (R = 1(*E*)-propenyl), 86993-82-0; **22** (R = 2-methyl-1-propenyl), 87011-58-3; **22** (R = 2(*E*)-but-2-enyl), 87011-59-4; **23** (R = isopropenyl), 86993-88-6; **23** (R = 2-methyl-1-propenyl), 86993-89-7.

Alkylation of the Stilbene Dianion

James G. Smith,* Edward Oliver, and Thomas J. Boettger

Guelph-Waterloo Centre for Graduate Work in Chemistry, Department of Chemistry, University of Waterloo, Waterloo, Ontario N2L 3G1, Canada

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The stilbene dianion, **2**, formed by reducing stilbene, **1**, with alkali metals, was alkylated with methyl halides, isopropyl halides, and *tert*-butyl halides. In the case of the primary and secondary alkyl halides, the alkylation products were found to vary markedly with the leaving group and, to a lesser extent, with the cation associated with **2**. This variation was rationalized on the basis of competitive mechanisms involving nucleophilic substitution and single electron transfer. The product mixtures formed with *tert*-butyl halides were especially complex. Alkylation products containing a 1,4-cyclohexadiene ring were isolated and characterized.

Anionic species derived by the reductive metalation of unsaturated substrates with alkali metals have been of synthetic[1] and mechanistic[2] interest since the early investigations of Schlenk[3] and co-workers. Insofar as the reactions of these anionic derivatives with alkyl halides are concerned, evidence has accumulated that these reactions can proceed by mechanistic routes other than nucleophilic substitution. This has been clearly substantiated[2] in mechanistic studies with the radical anion of naphthalene. Electron transfer from the radical anion to the alkyl halide leads to formation of an alkyl radical. Subsequent combination of the alkyl radical with a second radical anion leads to an alkylated monoanion and, eventually, an alkylated dihydronaphthalene.

Similar conclusions have been reached[4] in the alkylation of the benzophenone[4a] radical anion and the anthracene[4b] radical anion with chiral alkyl halides.

Numerous substrates when reduced by alkali metals form (monomeric) dianions rather than radical anions. Mechanistic studies[5,6] of their alkylations also indicate that

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[1] Kalyanaraman, V.; George, M. V. *J. Organomet. Chem.* **1973**, *47*, 225.

[2] (a) Garst, J. F. *Acc. Chem. Res.* **1971**, *4*, 400. (b) Holy, N. L. *Chem. Rev.* **1974**, *74*, 243.

[3] (a) Schlenk, W.; Appenrodt, J.; Michael, A.; Tahl, A. *Chem. Ber.* **1914**, *47*, 473. (b) Schlenk, W.; Bergmann, E. *Justus Liebigs Ann. Chem.* **1928**, *463*, 1.

[4] (a) Hebert, E.; Mazaleyrat, J. P.; Welvart, Z. *J. Chem. Soc., Chem. Commun.* **1977**, 877. (b)Malissard, M.; Mazaleyrat, J. P.; Welvart, Z. *J. Am. Chem. Soc.* **1977**, *99*, 6933.

[5] (a) Smith, J. G.; Irwin, D. C. *J. Am. Chem. Soc.* **1980**, *102*, 2757. (b) Smith, J. G.; Mitchell, D. J. *Ibid.* **1977**, *99*, 5045.

[6] Garst, J. F.; Roberts, R. D.; Pacifici, J. A. *J. Am. Chem. Soc.* **1977**, *99*, 3528.

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Table I. Reaction Products Formed by Alkylation of 2 with Methyl Halides[a]

2, M =	RX, X =	products, R = Me						
		3	4	*rac*-7	*meso*-7	?	1	6
Li	Cl	7	4	61	22		6	
Li	Br	3	2	24	13	10	48	t
Li	I	7	2	15	6	7	55	8
Na	F	2	2	65	21	4	5	
Na	Cl	2	1	66	21	3	8	
Na	Br	5	1	22	11	14	46	1
Na	I	2	1	16	5	8	59	9
Na	SO_4	2	2	71	24	1	t	
K	Cl	5	2	43	16	5	29	t
K	Br	5	t	35	12	4	44	t
K	I	8	t	12	4	9	67	

[a] t = less than 1%.

electron transfer can be a component feature in this reaction. In addition, the alkylation results are affected by the particular halogen present as the leaving group. In summary, alkylation of a dianion (A^{2-}) by an alkyl halide that involves electron transfer proceeds as shown in eq 1 and 2. After the initial electron transfer from the dianion

$$A^{2-} + RX \rightarrow A^{-}\cdot + (RX)^{-}\cdot \xrightarrow{\text{fast}} R\cdot + X^{-} \qquad (1)$$

$$R\cdot + A^{-}\cdot \rightarrow (R\text{-}A)^{-} \qquad (2)$$

to the alkyl halide leading to the formation of the alkyl radical, facile interaction of the radical and radical anion can occur since both are formed in close proximity.

It is our purpose in this study to present experimental data on the alkylation of the stilbene dianion, 2, and to analyze these results from the viewpoint that electron transfer may be a factor. In this study, the leaving group of the alkyl halides was varied usually from chlorine through bromine to iodine. The alkyl group was also changed from methyl to isopropyl and *tert*-butyl and the counterions of 2 from lithium to sodium and potassium.

$PhCH{=}CHPh$

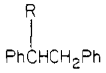
1

$[PhCH{=}CHPh]^{2-}2M^{+}$

2

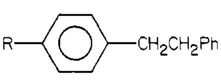
$PhCH_2CH_2Ph$

3

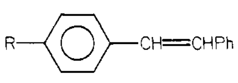


$PhCH(R)CH_2Ph$

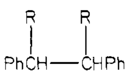
4[a]



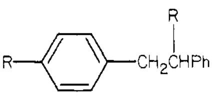
5[a]



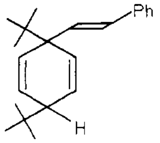
6[a]



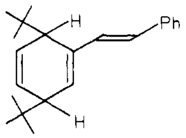
7[a]



8[a]



9[b]



10[b]

[a] **a**, R = Me; **b**, R = *i*-Pr; **c**, R = *t*-Bu. [b] Cis/trans assignments in the cyclohexadiene ring are uncertain.

Results

Methylation. The stilbene dianion has been reported to react with methyl iodide with chiefly stilbene being regenerated[3a] and low yields of alkylation products being isolated.[3a,7] In contrast to this, facile alkylation of the dianion occurred with dimethyl sulfate[7,8] and with alkyl chlorides.[9]

For this reason methyl fluoride, chloride, bromide, and iodide and dimethyl sulfate were compared as methylating agents for 2. Product mixtures were analyzed by gas chromatography, and the results are summarized in Table I.

It can be seen that alkylation of dianion 2 (M = Na) indeed occurred smoothly with methyl chloride and fluoride and dimethyl sulfate to produce chiefly the diastereomeric 2,3-diphenylbutanes in approximately a 3:1 rac/meso mixture. However, with methyl iodide the major product became regenerated *trans*-stilbene and relatively small amounts of alkylation occurred. Insofar as methyl chloride and iodide were concerned the same trend in alkylation was observed when lithium and potassium were counterions. The behavior of methyl bromide was variable—with lithium and sodium counterions, product mixtures similar to these produced by methyl iodide were obtained. But with potassium as the counterion, methyl bromide behaved much as methyl chloride.

A hitherto undetected alkylation product was isolated from the alkylation mixture produced by methyl iodide, *trans*-4-methylstilbene. This was never formed in more than trace amounts unless the leaving group was iodide. A second alkylation "product" was also formed in small amounts and isolated by preparative gas chromatography. However, further examination of this material by gas chromatography using different columns showed it to contain at least four components. Further efforts to identify these were not made.

Isopropylation. In a similar study, the dianion 2 (M = Li, Na, K) was alkylated with isopropyl chloride, bromide, and iodide. A somewhat different trend was noted as the leaving group changed from chloride to bromide to iodide (see Table II). While the amount of stilbene regenerated by the iodide was higher than when the chloride was used, the amount of stilbene never exceeded 21% of the reaction products. As was the case with methyl chloride, relatively smooth alkylation was effected with isopropyl chloride to form approximately a 1:1 mixture of the *rac*- and *meso*-2,5-dimethyl-3,4-diphenylhexanes. The most significant change in the alkylation products was the formation of increasing amounts of the ring-alkylated product 8 (R = *i*-Pr), 1-(*p*-isopropylphenyl)-3-methyl-2-phenylbutane, as the halogen changed. Indeed, with the alkyl iodide, a 1:1:1 mixture of 8 and *rac*- and *meso*-7 arose. Again, these alkylation results were not dependent on the counterion present with 2. Aside from the previously reported[9] monoalkylation product 4, 3-methyl-1,2-diphenylbutane, *trans*-*p*-isopropylstilbene was identified and the analogous dialkylated stilbene tentatively identified. Several other reaction products were present but in amounts so small that attempts to isolate them were not successful.

These two studies confirmed the earlier alkylation studies with dimethyl sulfate,[8] methyl iodide,[3a] and isopropyl chloride.[9] It is obvious that the leaving group present in the alkylation agent markedly affects the character of the alkylation products.

tert-Butylation. Since low yields of alkylation products had been isolated[9] from the alkylation of 2 with *tert*-butyl chloride, the above alkylation studies were extended to *tert*-butyl chloride and bromide. Quite complex reaction

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(7) Cabaret, M. D. *C. R. Hebd. Seances Acad. Sci., Ser. C* **1974**, *279*, 605.

(8) (a) Wright, G. F. *J. Am. Chem. Soc.* **1939**, *61*, 2106. (b) Myers, G. S.; Richmond, H. H.; Wright, G. F. **1947**, *69*, 710.

(9) Reesor, J. W. B.; Smith, J. G.; Wright, G. F. *J. Org. Chem.* **1954**, *19*, 940.

Table II. Reaction Products Formed by Alkylation of 2 with Isopropyl Halides

		products, R = *i*-Pr								
2, M =	RX, X =	3	4	1	*rac*-7	*meso*-7	8	b	6	other[a]
Li	Cl	7	6	3	31	28	4	6	9	6
Li	Br	1	2	33	31	31	9	6	4	13
Li	I	11	4	12	20	22	21	2	3	5
Na	Cl	2	5	2	35	47	4	1	1	3
Na	Br	2	6	4	23	28	13	5	9	10
Na	I	4	4	10	24	19	26	3	10	
K	Cl	4	11	t[c]	37	38	5	2	3	
K	Br	11	6	11	25	26	10	2	5	4
K	I	5	2	21	20	21	22	3	6	

[a] Unidentified peaks. [b] Tentatively identified as α,p'-diisopropylstilbene. [c] t = less than 1%.

mixtures were obtained, but all major products and some minor products were isolated and identified.

In agreement with the earlier report,[9] relatively small amounts of bibenzyl and regenerated *trans*-stilbene were found. The remaining products were mono- and dialkylated compounds, thus demonstrating a surprisingly efficient alkylation for tertiary halides.

Also, in agreement with the earlier study,[9] the major monoalkylated product (ca. 25%) was 3,3-dimethyl-1,2-diphenylbutane, **4** (R = *t*-Bu). However, in addition, *p-tert*-butylbibenzyl, **5** (R = *t*-Bu), and *trans-p-tert*-butylstilbene, **6** (R = *t*-Bu), were present; the latter was not unexpected in view of the results obtained on methylation and isopropylation.

The dialkylation products were, for the most part, of an unexpected structure. Small amounts of 1-(*p-tert*-butylphenyl)-3,3-dimethyl-2-phenylbutane, **8** (R = *t*-Bu), were present, but the major dialkylation product was assigned structure **9**. This assignment was based largely on the ^{1}H NMR spectrum that showed the presence of five aromatic protons, four equivalent vinyl protons, two coupled (J = 16 Hz, trans) vinyl protons, and one additional proton at δ 2.4. The IR spectrum confirmed the presence of both cis and trans double bonds.

The formation of 2,5-cyclohexadiene alkylation products is not without precedence,[10] and the formation of such products has been suggested as precursors to the ring-alkylation products that are isolated in other alkylation reactions.

A second minor dialkylation product was isolated readily because of its low solubility and high melting point (140 °C). This product had been reported[9] earlier and tentatively identified as 2,2,5,5-tetramethyl-3,4-diphenylhexane, **7C**. However, both diastereomers[11] of this hydrocarbon were recently prepared and neither had the reported melting point. The ^{1}H NMR spectrum showed five aromatic protons, two vinyl protons in a trans relationship as well as three additional vinyl protons and two aliphatic protons with a complex coupling pattern. Decoupling experiments showed that the two aliphatic protons were coupled to one another (J = 5 Hz) as well as to the three vinyl protons. Structure **10** is proposed for this compound. Precedence[12] exists in the literature for the sizeable long-range coupling constant observed for the two 1,4-aliphatic protons in this 2,5-cyclohexadiene derivative.

UV spectra of **9** and **10** were in accord with the proposed structures. Compound **9** showed a λ_{max} at 250 nm similar to styrene (244 nm) while **10** with its more conjugated system had a λ_{max} at 286 nm (cf. *trans*-1-phenyl-1,3-butadiene, 280 nm).

Discussion

It is generally acknowledged[13] that the opportunity for electron transfer increases with the ease of reduction of the carbon–halogen bond. Thus alkyl iodides should experience it the most and chlorides the least. The changing nature of the alkylation products from the stilbene dianion and methyl or isopropyl halides can be attributed to the increased degree of electron transfer with the alkyl iodides relative to the chlorides. Why then with methyl iodide, stilbene formation dominates but with isopropyl iodide a different alkylation product, **8b**, is formed? Sargent[14] has noted an increase in alkylation of sodium naphthalenide as the alkyl group changed from primary to secondary to tertiary. His explanation is applicable here. As the reduction potential of the alkyl radical increases from methyl to isopropyl, less reduction of the alkyl radical to its anion ($R\cdot \rightarrow R{:}^-$) by the concomitantly formed stilbene radical anion and more alkylation (radical anion–radical coupling) occurs. The appearance of the para-alkylation product **8** (R = *i*-Pr) is an expected consequence of radical anion–radical coupling as has been noted elsewhere.[5]

Reactions of the benzophenone anil dianion with primary alkyl bromides and iodides have been shown[5] to proceed to a large extent by electron transfer. However, with primary alkyl chlorides no evidence for an electron-transfer process was obtained although alkylation did proceed. Since reaction between the stilbene dianion, **2**, and methyl or isopropyl chloride produced chiefly the α,α'-dialkylbibenzyls **7** (R = Me or *i*-Pr), it is suggested that these alkylations proceeded chiefly by nucleophilic substitution, the dianion being insufficiently strong a reducing agent to reduce rapidly the carbon–chlorine bond. Since alkylation of **2** (M = Na) with methyl fluoride or dimethyl sulfate produced product mixtures almost identical with that obtained with methyl chloride, it is suggested that these reactions proceed in the same mechanistic manner as methyl chloride.

It has been observed elsewhere[5a] that with primary alkyl bromides and iodides the extent of electron transfer depends in part on the counterion associated with the dianion. Electron transfer decreased as one proceeded from lithium to sodium to potassium. Quantitatively, this aspect has been examined with the reaction between alkali-metal naphthalenides and 5-hexenyl fluoride.[15] In this case the reaction of lithium naphthalenide was at least 10^4 times faster than the analogous potassium compound. With the assumption that such a situation prevailed here, then the slower rate of the electron-transfer reaction with **2** (M = K) relative to **2** (M = Li or Na) would permit nucleophilic

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(10) Lindow, D. F.; Harvey, R. G. *J. Am. Chem. Soc.* **1971**, *93*, 3786.

(11) Hellman, G.; Beckhaus, H. D.; Rüchardt, C. *Chem. Ber.* **1979**, *112*, 1808.

(12) (a) Durham, L. J.; Studebaker, J.; Perkins, M. J. *J. Chem. Soc., Chem. Commun.* **1965**, 456. (b) Paschal, J. W.; Rabideau, P. W. *J. Am. Chem. Soc.* **1974**, *96*, 272. (c) Cheetham, A. K.; Grossel, M. C.; Newsam, J. M. *Ibid.* **1981**, *103*, 5363.

(13) Bank, S.; Juckett, D. A. *J. Am. Chem. Soc.* **1976**, *98*, 7742.

(14) Sargent, G. D.; Lux, G. A. *J. Am. Chem. Soc.* **1968**, *90*, 7160.

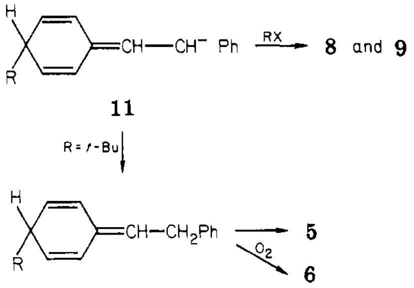
(15) Garst, J. F.; Barton, F. E. *J. Am. Chem. Soc.* **1974**, *96*, 523.

substitution reactions to intrude significantly in the case of the reaction between methyl bromide and **2** (M = K) but electron transfer would dominate with **2** (M = Li or Na).

Do alkyl chlorides react with **2** *entirely* by nucleophilic substitution? In the case of radical anions, competitive nucleophilic substitution–electron-transfer processes have been suggested. In the case of the isopropyl halides, ring-alkylated products **8** and **6** (R = *i*-Pr) are formed in small but significant amounts. Whether this is due to some electron-transfer competing with nucleophilic substitution or whether it is a reflection of the delocalization of the benzylic type anion cannot be decided at this point.

The reaction of the stilbene dianion, **2**, with *tert*-butyl halides produced somewhat different results than those observed with other alkyl halides. The reaction mixtures were very similar whether the leaving group was chloride or bromide. It is suggested that, in this case, electron transfer is responsible for the alkylation since nucleophilic substitution with *tert*-butyl chloride is so slow. Indeed, the alkylation reaction with *tert*-butyl chloride is unusually slow requiring several hours at 20 °C before the characteristic color of **2** fades.

The interesting alkylation product **9** can be rationalized by radical anion–radical reaction to produce the para-alkylated anion **11** that can react with a second *tert*-butyl halide to provide **8** (after a [1,4] sigmatropic rearrangement of H) or **9** by a shift of the anionic charge and alkylation at the 1-position of the 2,5-cyclohexadiene ring. Protonation of **11** provides the precursor to both **5** (H migration) and **6** (oxidation during isolation). The formation of **10** can be accounted for in a similar manner beginning with an ortho-alkylated analogue of **11**. Preference for para-alkylation obviously arises from the steric bulk of the *tert*-butyl group.



The total amount of dialkylation products (40–50% usually) is surprisingly high. It has been assumed that the second alkylation step proceeds by nucleophilic substitution[2,14] so that with a tertiary halide low yields of dialkylated products would be expected. However, it has been reported[16] recently that sodium naphthalenide and *tert*-butyl chloride produced substantial amounts[17] of the di-*tert*-butyldihydronaphthalene. The suggestion was made that this second alkylation is also an electron-transfer process with *tert*-butyl halide and this suggestion seems applicable here.

One interesting observation was made on treating the stilbene dianion **2** (M = Na) with 1 equiv of either isopropyl chloride or isopropyl iodide. The alkylation with isopropyl chloride produced chiefly the monoalkylated species **4** (R = *i*-Pr). With isopropyl iodide, chiefly dialkylation occurred and half the original stilbene was recovered as bibenzyl. The alkyl chloride reaction proceeded sufficiently slowly at −70 °C by nucleophilic substitution that proper mixing of the reagents occurred and stepwise alkylation resulted. Alkyl iodides react very rapidly[13] by electron-transfer processes, and it is suggested that alkylation occurred at locally high concentrations of the alkyl iodide as it was added and before mixing could occur.

One aspect of these alkylations is puzzling and merits further investigation. The dianion **2** should be a relatively strong base as well as a nucleophile. However, the degree of dehydrohalogenation shown in alkylations with isopropyl and *tert*-butyl halides is surprisingly small. This observation suggests that a more quantitative evaluation of the basicity of these anionic species is warranted.

Experimental Section

Melting points were measured with a Mel-temp apparatus and are uncorrected. Infrared spectra were recorded on a Beckmann IR-10 spectrometer, and NMR spectra were determined on a Varian T-60 or Brucker WP-80 spectrometer using $CDCl_3$ solutions with chemical shifts reported in δ units downfield from internal tetramethylsilane. UV spectra were recorded on a Unicam SP-800 spectrophotometer. Analyses were performed by MHW Laboratories, Phoenix, AZ. The gas chromatographic analyses were reproducible on a run-to-run basis within ±5% of the reported values.

General Alkylation Procedure. The stilbene dianion **2** was prepared by shaking a solution of stilbene (1.8 g, 0.01 mol) in 100 ± 10 mL of tetrahydrofuran (freshly distilled under nitrogen from $LiAlH_4$) with excess freshly cut sodium (or lithium, potassium) metal in a Schlenk tube[9] for 8 h. The solution of **2** was drained from the excess metal under nitrogen into a nitrogen-filled flask equipped with a side neck closed by a septum. The flask was cooled in a dry ice–2-propanol bath and an excess of the reagent (0.025 mol) injected through the septum while the solution was stirred (magnetic bar stirrer). Except for the *tert*-butyl chloride and methyl fluoride, color changes were immediately apparent. After 1 h at −70 °C, the solution was allowed to warm to room temperature and stirred until decolorization was complete.

In the case of methyl chloride and fluoride, the gases were condensed in a tared vessel and allowed to distill from this through the side neck into the solution of **2** cooled to −70 °C.

Isolation. The final reaction mixture was treated with water (~250 mL), and the reaction products were isolated by extraction with diethyl ether. The ether extract was concentrated and analyzed by gas chromatography or chromatographed as described below.

Alkylation Products Formed on Methylation. The reaction mixtures were analyzed on an F and M Model 700 gas chromatograph equipped with flame ionization detectors. A 5 ft by $^1/_4$ in. column packed with 15% SE-52 on 80–100 mesh Chromosorb W operated at 150 °C was employed. The various peaks were identified by "spiking" a sample with known compounds previously isolated[8] from these reactions.

The products eluted in the following order (relative retention time): bibenzyl, **3**, (1.00); α-methylbibenzyl, **4**, R = Me (1.15); *rac*-2,3-diphenylbutane, *rac*-**7**, R = Me (1.33); *meso*-2,3-diphenylbutane, *meso*-**7**, R = Me (1.49); unknowns (1.70, 1.90); *trans*-stilbene, **1** (2.12); *trans*-4-methylstilbene, **6**, R = Me (3.51). Analytical results are summarized in Table I.

trans-4-Methylstilbene, **6**, was isolated by dissolving the reaction product from disodium stilbene (**2**, M = Na) and methyl iodide (1.80 g) in 100 mL of hot hexane. On cooling, *trans*-stilbene (0.75 g, mp 115–120 °C) crystallized; the filtrate containing **6** was concentrated and chromatographed on alumina (Woelm basic grade I) by using hexane graded to 1:1 benzene–hexane. The material eluting with the first 200 mL of solvent (0.59 g) consisted of **3**, **4**, and **7** (GC) and was not investigated further. Thereafter a mixture of stilbene and 4-methylstilbene (0.40 g) was collected. This mixture was separated by preparative GC using an Aerograph Autoprep apparatus and a 30 ft by $^3/_8$ in. column packed with 30% SE-52 on 60–80 mesh Chromosorb W operated at 235 °C with a carrier gas flow rate of 150 mL/min. The 4-methylstilbene collected (0.10 g) was recrystallized from ethanol: 80 mg; mp 110–112 °C, mixture melting point with authentic material

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[16] Holy, N. L.; Vail, H. P.; Nejad, A. H.; Huang, S. J.; Marshall, J. L.; Saracoglu, D.; McDaniel, C. R., Jr. *J. Org. Chem.* **1980**, *45*, 4271.

[17] A 30% yield is based on the naphthalene consumed in the alkylation.

Table III. Reaction Products Formed by Alkylation of 2 with *tert*-Butyl Halides[a]

		products, R = *t*-Bu								
RX, X =	cation, M$^+$, M =	3	4	1	5	8	9	6	10	other
Cl	Li	8	22	4	1	3	32	14	6	10
Cl	Na	4	23	6	4	12	36	9	6	
Cl	K	3	33	5	12	6	23	9	1	8
Br	Li	1	30	t	2	10	29	22	3	3
Br	Na	0.5	28	t	4	10	41	10	6	0.5
Br	K	t	32	2	4	9	38	10	4	1

[a] t = less than 1%.

111-113 °C. The NMR and IR spectra of the isolated material were identical with those of the authentic compound.

Alkylation Products Formed on Treating 2 with Isopropyl Halides. The reaction mixtures were analyzed on an F and M Model 810 gas chromatograph equipped with FID detectors, using a 6 ft by $^1/_8$ in. column packed with 10% SE-30 on 80–100 mesh Chromosorb W and operated at 160 °C with a carrier gas flow rate of 40 mL/min. While the diastereomeric 2,5-dimethyl-3,4-diphenylhexanes, 7 (R = *i*-Pr), were generally the major products, several other compounds were present. "Spiking" the reaction mixtures with compounds previously isolated[9] enabled the GC peaks corresponding to bibenzyl, 3, 3-methyl-1,2-diphenylbutane, 4 (*R* = *i*-Pr), *trans*-stilbene, 1, *rac*- and *meso*-2,5-dimethyl-3,4-diphenylhexane, 7 to be identified.

Following the elution of *meso*-dimethyldiphenylhexane, three additional peaks eluted which in some experiments were formed in significant amounts. These peaks (designated A, B, and C in order of election) were collected on an Aerograph Autoprep Model 700, preparative gas Chromatograph using a 20 ft by $^3/_8$ in. column packed with 10% QF-1 on 60–80 mesh Chromosorb W and operated at 170 °C with a carrier gas flow of 150 mL/min.

Peak A provided an oil whose NMR and IR spectra were identical with those of *α,p′*-diisopropylbibenzyl, 8 (R = *i*-Pr). Peak B also provided an oil that was tentatively identified as *α,p′*-diisopropylstilbene on the basis of its retention time compared to that of an authentic sample. The amount isolated was insufficient for a spectral characterization. Peak C provided a solid, mp (from ethanol) 88–89 °C, which was not depressed on admixture with authentic *trans*-4-isopropylstilbene, 6 (R = *i*-Pr). Spectral properties (IR and NMR) were identical with those of the authentic stilbene.

The compounds eluted in the following order (relative retention time): bibenzyl (1.0); 3-methyl-1,2-diphenylbutane (1.87); *trans*-stilbene (2.15); *rac*-2,5-dimethyl-3,4-diphenylhexane (3.49); *meso*-2,5-dimethyl-3,4-diphenylhexane (4.20); *α,p′*-diisopropylbibenzyl (4.85); *α,p′*-diisopropylstilbene (5.32); *trans*-4-isopropylstilbene (7.08). Several additional compounds were detected by GC in small amounts but were not investigated further. Analytical results are summarized in Table II.

Reference Compounds. Isopropyl Products. *α,p′*-Diisopropyldesoxybenzoin. *p*-Isopropyldesoxybenzoin (3.9 g, 0.012 mol) was refluxed under nitrogen, in 30 mL of toluene with 0.5 g (0.013 mol) of sodamide for 8 h. After being cooled, the suspension was treated with 2.0 g (0.016 mol) of isopropyl bromide and refluxed for an additional 10 h. The organic layer was washed with water, dried ($MgSO_4$), and evaporated and the residue recrystallized from methanol to give 2.8 g (83%) of *α,p′*-diisopropyldesoxybenzoin: mp 84–86 °C; NMR (CCl_4) δ 0.73 and 0.98 (two d's, *J* = 7 Hz, 6 H), 1.18 (d, *J* = 6 Hz, 6 H), 2.0–3.1 (m, 2 H), 4.08 (d, *J* = 10 Hz, 1 H), 6.9–7.4 (m, 7 H), 7.86 (half of ABq, *J* = 9 Hz, 2 H); IR (KBr) 1660, 1600, 810, 730, 700 cm^{-1}. Anal. Calcd for $C_{20}H_{24}O$: C, 85.67; H, 8.64. Found: C, 85.53; H, 8.69.

***α,p′*-Diisopropylbibenzyl, 8 (R = *i*-Pr).** *α,p′*-Diisopropyldesoxybenzoin (1.1 g, 4 mmol) in 20 mL of pentane was added to 8 g of amalgamated zinc, 20% HCl (40 mL) was added, and the mixture was refluxed for 3 h. The organic layer was washed with water, dried ($MgSO_4$), and evaporated and the residue distilled: bp 142–143 °C (0.2 mm); 0.85 g (81%). An analytical sample was obtained by preparative gas chromatography: NMR (CCl_4) δ 0.76 and 0.99 (two d's, *J* = 7 Hz, 6 H), 1.16 (d, *J* = 7 Hz, 6 H), 1.6–2.3 (m, 1 H), 2.3–3.3 (m, 4 H), 6.7–7.3 (m, 9 H); IR (neat) 2980, 1470, 1460, 1390, 1370, 830, 750, 700 cm^{-1}. Anal. Calcd for $C_{20}H_{26}$: C, 90.14; H, 9.85. Found: C, 90.41; H, 9.57.

***p*-Isopropyldesoxybenzoin.** The title compound was prepared by using a procedure described for related compounds,[18] from 15.5 g (0.1 mol) of phenacetyl chloride, 48.0 g (0.4 mol) of cumene, and 16.0 g (0.12 mol) of aluminum chloride in 100 mL of carbon disulfide. The crude product was distilled, bp 115–120 °C (0.1 mm), giving 14.5 g (76%) of 4-isopropyldesoxybenzoin: mp 42.5–43.5 °C; NMR (CCl_4) δ 1.26 (d, *J* = 7 Hz, 6 H), 2.6–3.3 (m, 1 H), 4.17 (s, 2 H), 7.1–7.5 (m, 7 H), 7.91 (half of ABq, *J* = 9 Hz, 2 H); IR (neat) 1680, 1620, 1280, 820, 720 cm^{-1}. Anal. Calcd for $C_{17}H_{18}O$: C, 85.65; H, 7.63. Found: C, 85.52; H, 7.69.

***α,p′*-Diisopropylstilbene.** *α,p′*-Diisopropyldesoxybenzoin (3.0 g, 0.013 mol) was reduced with 1 g of lithium aluminum hydride in 90 mL of diethyl ether. After hydrolysis of the reaction product with water, then dil. HCl, the product was isolated by ether extraction. After the ether extract was dried ($MgSO_4$) and concentrated, the residue was distilled: 2.4 g (76%); bp 147–149 °C (0.05 mmHg). Dehydration of the expected alcohol had evidently occurred during isolation: NMR (CCl_4) δ 1.08 and 1.12 (two d's, *J* = 6 Hz, 6 H), 2.4–3.0 (m, 2 H), 6.37 (s, 1 H), 6.7–7.4 (m, 9 H); IR (neat) 2908, 1510, 1470, 890, 830, 780 700 cm^{-1}. Analysis of this material by GC showed it to be 90% one component with small amounts of three other compounds being present.

***trans*-*p*-Isopropylstilbene, 6 (R = *i*-Pr).** The alcohol 1-(4-isopropylphenyl)-2-phenyl-1-ethanol (mp 42–42.5 °C, prepared[19] in 69% yield from 4-isopropylbenzaldehyde and benzylmagnesium chloride) was dehydrated in refluxing xylene by using a catalytic amount of *p*-toluenesulfonic acid to give *trans*-4-isopropylstilbene, mp 88–80 °C (from methanol),[17] in 74% yield.

Alkylation Products Formed on Treating 2 with *tert*-Butyl Halides. The reaction mixture obtained from the stilbene dianion and the *tert*-butyl halides were analyzed on a Hewlett-Packard 5840 gas chromatograph using a 6 ft by $^1/_8$ in. column packed with 4% OV-101 plus 6% OV-210 on 100–120 mesh HP Chromosorb W. A temperature program was used—initial temperature 100 °C for 2 min, rate of temperature increase 3 °C/min to 200 °C, and this temperature held for 15 min. The identified reaction products eluted in the following order (relative retention time): bibenzyl, 3 (0.70); 4, R = *t*-Bu (0.93); stilbene, 1 (1.0); 5, R = *t*-Bu (1.07); 8, R = *t*-Bu (1.33); 9, R = *t*-Bu (1.49); 6, R = *t*-Bu (1.57); 10, R = *t*-Bu (1.66). The analyses are summarized in Table III.

Isolation of the tert-Butylated Alkylation Products. The reaction product from a potassium/*tert*-butyl bromide experiment was distilled and the fraction with a boiling point of 105–125 °C at 0.3 mm collected (0.68 g, a lower boiling fraction was chiefly bibenzyl). GC analysis showed that this fraction was chiefly the product with a relative retention time (rrt) of 0.93 with some product of rrt 1.07. The residue (1.64 g) contained the products with longer rrt. The major components of the distillate were separted by preparative gas chromatography (PGC). PGC was performed on a Varian 1520 gas chromatograph using a 5 ft by $^3/_8$ in. column containing 3% SE-30 on 60–80 mesh Chromosorb W at 140 °C with a helium flow rate of 75 mL/min. The compound, rrt 0.93, was 3,3-dimethyl-1,2-diphenylbutane (4, R = *t*-Bu): NMR δ 0.96 (s, 9 H), 2.5–3.3 (m, 3 H), 6.9–7.3 (m, 10 H); IR (neat) 3040, 2960, 1500, 1450, 1365, 745, 720, 690 cm^{-1}. On storage, this material crystallized and after recrystallization from 30–60 °C petroleum ether melted at 30–35 °C (lit.[9] 34–37 °C).[9] The second component of the distillate, rrt 1.07, was *p*-*t*-butylbibenzyl, 5 (R

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(18) Buck, J. S.; Ide, W. S. *J. Am. Chem. Soc.* **1932**, *54*, 3012.

(19) Balla, E. *C. R. Hebd. Seances Acad. Sci.* **1934**, *198*, 947.

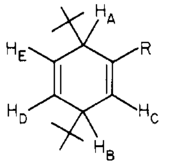
= *t*-Bu): oil; NMR δ 1.34 (s, 9 H), 2.95 (s, 4 H), 7.2–7.5 (m, 9 H); IR (neat) 3040, 2960, 1520, 1510, 1450, 1365, 1270, 820, 750, 690 cm^{-1}. This material was spectroscopically identical with an authentic sample prepared by hydrogenation of *trans-p-tert*-butylstilbene. On standing, the sample crystallized; mp (from 30–60 ° petroleum ether) 34–35 °C. Anal. Calcd for $C_{18}H_{22}$: C, 90.69; H, 9.31. Found: C, 91.01; H, 9.07.

The distillation residue was chromatographed on silica gel eluting with 30–60 °C petroleum ether, collecting 100-mL fractions and analyzing each fraction by GC. Fractions 8–10 crystallized, and all contained substantial quantities of the compound with rrt 1.57. These were combined (0.28 g) and recrystallized twice from methanol: 0.11 g, mp 96–98 °C,[21] mixture melting point with authentic *trans-p-t*-butylstilbene, **6** (R = *t*-Bu), was the same; NMR δ 1.35 (s, 9 H), 7.15 (s, 2 H), 7.25–7.65 (m, 9 H); IR (Nujol) 970, 960, 815, 750, 685 cm^{-1}.

Fraction 7 (0.19 g) was chiefly the compound with rrt 1.33 and was purified by preparative gas chromatography at 170 °C: an oil; NMR δ 0.95 (s, 9 H), 1.23 (s, 9 H), 2.5–3.3 (m, 3 H), 6.85 and 7.12 (ABq, J = 9 Hz, 4 H), 7.15 (s, 5 H); IR (neat) 2960, 1480, 1460, 1400, 1370, 830, 810, 740, 720, 700 cm^{-1}. This product was identified as 1-(*p-t*-butylphenyl)-2-phenyl-3,3-dimethylbutane (**8**, R = *t*-Bu).

Fraction 5, a solid (53 mg), corresponded to the material with rrt 1.66. It was recrystallized from methanol to give 18 mg of **10**: mp 135–137 °C; NMR 0.93 (s, 9 H), 0.97 (s, 9 H), 2.4–2.6 (m, 1 H, H_A), 2.8–3.1 (m, 1 H, H_B), 6.0–6.1 (m, 2 H, H_C and H_D), 6.2–6.3 (m, 1 H, H_E), 6.48 and 6.86 (ABq, J = 17 Hz, 2 H), 7.1–7.6 (m, 5 H).

Irradiation of H_E collapsed H_A to a doublet, J = 5 Hz and simplified the H_C, H_D signal. Further decoupling experiments showed that H_A and H_B were coupled to one another and to H_C and/or H_D. Tentative assignments are



R = *trans*-CH=CHPh

IR (Nujol): 1360, 950, 740, 680 cm^{-1}. UV (MeOH): λ_{max} (ϵ) 286 (2.4 × 10^4), 306 nm (sh, 1.6 × 10^4). Anal. Calcd for $C_{22}H_{30}$: C, 89.71; H, 10.29. Found: C, 89.90; H, 10.12.

Fraction 4 consisted chiefly of the minor product with rrt 2.23. It was further purified by preparative GC at 185 °C to give an oil: NMR δ 0.82 and 0.85 (two s, 18 H), 2.08 (d, J = 5 Hz, 1 H), 2.50 (br s, 1 H), 5.8–6.2 (m, 3 H), 6.48 and 6.88 (ABq, J = 16 Hz, 2 H), 7.1–7.6 (m, 5 H). This compound was unstable on storage and has yet to be identified.

The reaction mixture from **2** (M = Li, two *t*-BuBr) was similarly treated (distilled, the residue chromatographed). The first material that eluted on chromatography (fraction 3, 0.58 g) was twice recrystallized from methanol to give 0.20 g of **9**: mp 61–64 °C; NMR 0.91 and 0.96 (two s, 18 H), 2.40 (s, 1 H), 5.93 (s, 4 H), 4.35 and 4.65 (ABq, J = 16 Hz, 2 H), 7.2–7.7 (m, 5 H); IR (Nujol) 1400, 1360, 1220, 970, 860, 740, 690 cm^{-1}; UV (MeOH) λ_{max} (ϵ) 250 nm (2.1 × 10^4). Anal. Calcd for $C_{22}H_{30}$: C, 89.71; H, 10.29. Found: C, 90.00; H, 10.24.

Reaction with 1 mol of Isopropyl Halide. The general procedure described earlier was followed except for the reduced amount of isopropyl halide. A sample was withdrawn from the reaction mixture after a 30-min reaction at −70 °C and quenched in methanol. GC analyses gave the following results: (i) with 1 mol of isopropyl chloride, 82% 3-methyl-1,2-diphenylbutane, **4** (R = *i*-Pr), 11% bibenzyl, **3**, and 7% *trans*-stilbene, **1**; (ii) with 1 mole of isopropyl iodide, 3% 3-methyl-1,2-diphenylbutane, **4** (R = *i*-Pr), 15% *dl*-**7** (R = *i*-Pr), 10% *meso*-**7** (R = *i*-Pr), 10% **8** (R = *i*-Pr), 48% bibenzyl, **3**, and 6% *trans*-stilbene, **1**.

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Registry No. (*E*)-**1**, 103-30-0; **3**, 103-29-7; **4b**, 5814-85-7; **4c**, 53759-76-5; **5c**, 56767-93-2; **6a**, 1860-17-9; **6b**, 40231-48-9; **6c**, 20374-76-9; *rac*-**7a**, 2726-21-8; *mess*-**7a**, 4613-11-0; *rac*-**7b**, 64986-18-1; *meso*-**7b**, 64985-92-8; **8b**, 86943-92-2; **8c**, 86943-93-3; **9**, 86943-94-4; **10**, 86943-95-5; *p*-isopropyldesoxybenzoin, 1026-81-9; α,*p*-diisopropyldesoxybenzoin, 86943-96-6; phenacetyl chloride, 103-80-0; cumene, 98-82-8; 1-(4-isopropylphenyl)-2-phenyl-1-ethanol, 60313-22-6; α,*p*′-diisopropylstilbene, 86943-97-7.

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[20] mp 90–91 °C: Heck, R. F. *J. Am. Chem. Soc.* **1968**, *90*, 5518.

[21] mp 96–97 °C: Brook, A. G.; Pannell, K. H.; Anderson, D. G. *J. Am. Chem. Soc.* **1968**, *90*, 4374.