presence and in the absence of micellar surfactants have also been determined (Table VI). Cationic micellar CTAB enhances the equilibrium constant for the formation of **4** and **5** by factors of 4750 and 252, respectively, while NaLS and Igepal do not affect it. Since the rate constants for the formation of spiro complexes, k_1, are dependent on the hydroxide ion concentration, the observed micellar effects are composites of those on the parent glycol ethers **6** and **7** and those on the hydroxide ion. The effective hydrogen ion concentration at the micellar surface, however, may differ appreciably from that in the bulk phase.[5] The considerably more pronounced micellar effect on the rate of the acid-catalyzed decomposition of **1** than that on its neutral decomposition substantiate this observation. The interpretation of this and similar results in buffered solutions is complicated by the uncertainties in the pH of these solutions.[5] Combination of the values for k_{-1} and K for the spiro complex **5** in the absence and presence of CTAB (Tables III and VI) allows the calculation of the rate constants for the formation of **5** ($k_1^{H_2O}$ = 80 l. mol^{-1} sec^{-1}, k_1^{CTAB} = 31 l. mol^{-1} sec^{-1}). Micellar CTAB thus decreases the rate constant for the formation of **5** by a factor of 2.6, whereas it catalyzes the hydroxydehalogenations of dinitrosubstituted arenes by factors of *ca.* 60–80.[4] These micellar effects are not unexpected based on electrostatic considerations since the rate of the former reaction, which involves the internal cyclization of the naphthyl glycolate anion, would predictably be retarded in the presence of cationic micelles due to partial charge neutralization. The latter case, however, is a typical example of the effect of cationic micelles on a reaction between a solubilized neutral organic molecule and a small high-charge density anion.[4,5] The unusually large increase in the equilibrium constant for the formation of **5** is, of course, the consequence of the micellar enhancement of the rate of formation, k_1, and the micellar retardation of the rate of decomposition. Combining k_{-1} and K values for the influence of Igepal CO-730 on complex **5**, one estimates that this nonionic surfactant somewhat unexpectedly decreases the rate constant for the formation of the complex. Qualitatively, the effects of ionic micelles on the rates of Meisenheimer complex decomposition are explicable in terms of simple electrostatic interactions, however the rate retardation caused by nonionic surfactants cannot be accounted for solely in simple electrostatic terms, and evnironmental effects, such as hydrophobic and hydrogen bonding interactions, must be invoked to rationalize the observed effects.

Although specific steric effects clearly complicate the interpretation of the results for the spiro complexes **4** and **5**, it is evident that micelles affect both the initial and transition states for the formation and the decomposition of intermediates which are involved in nucleophilic aromatic substitution and that this dependence is very much influenced by the nature of the substrates and intermediates.

Registry No.—**1**, 12275-58-0; **2**, 29472-26-2; **3**, 29472-29-5; **4**, 1280-24-6; **5**, 29472-28-4.

Ionic *vs.* Free-Radical Additions with Opportunity for Phenyl Migration. Solvent Effects[1]

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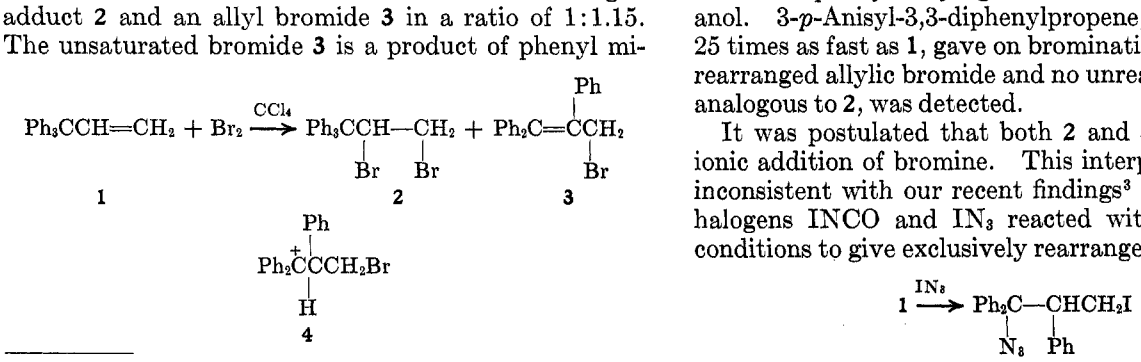
Addition of bromine azide to 3,3,3-triphenylpropene (**1**) proceeds with phenyl migration under ionic conditions (major product, **7**) but without phenyl migration under free-radical conditions (major product, **9**). The two products resulting from bromination of **1** were shown to derive from simultaneous ionic and free-radical addition processes. Addition of BrN_3 to 3,3-diphenylpropene (**10**) in polar solvents also proceeds with phenyl migration. The regiochemistry indicates steric control in the BrN_3 addition. Solvent effects of a different nature were observed during phenyl migration in the IN_3 addition to 3,3-diphenylpropene (**10**) and are interpreted in conjunction with three-membered-ring iodonium ion opening.

Recently Norman and coworkers[2] have shown that addition of bromine to 3,3,3-triphenylpropene (**1**) in carbon tetrachloride solution leads to a nonrearranged adduct **2** and an allyl bromide **3** in a ratio of 1:1.15. The unsaturated bromide **3** is a product of phenyl migration and probably arose from an intermediate of type **4** by loss of a proton. Norman, *et al.*, were in fact able to trap **4** by carrying out the bromination in methanol. 3-*p*-Anisyl-3,3-diphenylpropene, which reacts 25 times as fast as **1**, gave on bromination in CCl_4 only a rearranged allylic bromide and no unrearranged adduct, analogous to **2**, was detected.

It was postulated that both **2** and **3** result from an ionic addition of bromine. This interpretation seemed inconsistent with our recent findings[3] that the pseudohalogens INCO and IN_3 reacted with **1** under ionic conditions to give exclusively rearranged adducts (*cf.* **5**).



(1) Stereochemistry. LXI. For paper LX, see A. Hassner, *Accounts Chem. Res.*, **4**, 9 (1971).

(2) R. O. C. Norman and C. B. Thomas, *J. Chem. Soc. B*, 598 (1967).

(3) A. Hassner and J. S. Teeter, *J. Org. Chem.*, **35**, 3397 (1970).

At the same time we have shown[4] that bromine azide (BrN_3) in its additions to olefins is capable of both ionic and free-radical behavior, the latter being favored by solvents of low polarity. Hence, it became important to consider that bromine addition to **1** in CCl_4 may have proceeded by a dual mechanism, one leading to a rearranged, the other to a nonrearranged product.

Though the formation of the nonrearranged 1,2-dibromide **2** could be explained by fast trapping of an intermediate radical **6**, one cannot *a priori* assign the

$$Ph_3CCHCH_2Br$$
6

formation of **2** to a free-radical addition since there are abundant examples in the literature[5] of phenyl migration to a β radical, for instance, eq 1.[5a]

$$Ph_3CCH_2CH(=O) \xrightarrow[\Delta]{\text{peroxide,}} (Ph_3CCH_2) + CO \qquad (1)$$
$$\downarrow$$
$$Ph_2CHCH_2Ph$$

Results and Discussion

1. Additions to Triphenylpropene.—The behavior of bromide azide with triphenylpropene **1** was examined first since, unlike for bromine, the regiochemistry[6] of the products should be helpful in establishing the reaction pathway. Addition of BrN_3 in nitromethane–methylene chloride purged with oxygen to inhibit free-radical reaction gave primarily (86%) the rearranged 1,3-bromoazide **7** and a small amount (6%) of 2,3,3-triphenylallyl bromide **3**. The structure of **7** was obvious

$$Ph_3CCH{=}CH_2 \;(\mathbf{1}) + BrN_3 \xrightarrow[\text{ionic}]{CH_3NO_2,} Ph_2CCHCH_2Br \;(\mathbf{7}) + \mathbf{3}$$

7 $\xrightarrow{tert\text{-}BuO^-\,K^+,\ DMSO}$ $Ph_2C{=}C(Ph){-}C(=O)H$ (**8**)

from its nmr and mass spectra and from chemical reactions. Its nmr spectrum was very similar to that of the corresponding IN_3 adduct, including two aromatic peaks in a ratio of 13:2. The mass spectrum of **7** showed a base peak at *m/e* 180 ($Ph_2C{=}N^+$). A high-resolution mass spectrum confirmed the assignment of the base peak to a $C_{13}H_{10}N^+$ fragment. Like its iodo analog **5** bromo azide **7** was inert toward tertiary amines or potassium *tert*-butoxide in ether but was converted to triphenylacrolein **8** on treatment with potassium *tert*-butoxide in DMSO.

The formation of 6% of the allyl bromide **3** was unexpected since no corresponding product was found in the IN_3 addition to **1**; however, both **3** and **7** are the result of phenyl migration as expected from an ionic process.

(4) A. Hassner and F. Boerwinkle, *J. Amer. Chem. Soc.*, **90**, 216 (1968).

(5) (a) D. Y. Curtin and M. J. Hurwitz, *ibid.*, **74**, 5381 (1952); (b) S. Winstein and F. H. Senbold, *ibid.*, **75**, 2532 (1953); (c) P. D. Bartlett and J. D. Cotman, *ibid.*, **72**, 3095 (1950); L. H. Slaugh and J. H. Raley, *ibid.*, **82**, 1259 (1960); H. Meislich, J. Coustanza, and J. Streilitz, *J. Org. Chem.*, **33**, 3221 (1968).

(6) Regio is used to describe the directional effects in bond making or breaking: A. Hassner, *ibid.*, **32**, 2684 (1968).

The addition of BrN_3 to **1** in pentane in the presence of benzoyl peroxide and light proceeded much slower and led to the nonrearranged adduct **9** in 30% yield, in addition to 55% of unchanged olefin **1**.

$$Ph_3CCH{=}CH_2\;(\mathbf{1}) + BrN_3 \xrightarrow[\text{(radical)}]{\text{pentane}} Ph_3CCHCH_2N_3\;(\mathbf{9})$$
$$Ph_3CCHCH_2 \xrightarrow{BrN_3} \mathbf{9}$$
$$\downarrow N_3$$
10

The structure of **9** was obvious from the base peak in its mass spectrum at *m/e* 243 (Ph_3C^+) as well as minor peaks at *m/e* 270 ($M\cdot^+ - BrN_3$) and 284 [$M\cdot^+ - (N_2 + Br)$]. The absence of products resulting from phenyl migration indicates that in the free-radical addition of BrN_3 an intermediate radical (*i.e.*, **10**) is trapped by bromine azide faster than it can rearrange.

Backed by these results we reexamined the addition of Br_2 to triphenylpropene **1** in CCl_4. The results shown in Table I clearly indicate that the 1,2-dibromide **2** is a

TABLE I

PRODUCTS IN THE BROMINATION OF 3,3,3-TRIPHENYLPROPENE IN CCl_4

Conditions	Yield of products, %	
	2	**3**
48 hr, room light[a]	45	55
46 hr, dark, O_2	11	73
46 hr, dark, O_2	0	88
2,6-Di-*tert*-butylphenol		

[a] The procedure followed was that described in ref 2.

product of the free-radical addition of bromine to **1**, which is inhibited when the reaction is carried out in the presence of oxygen and of 2,6-di-*tert*-butylphenol. Hence, as in the case of BrN_3, ionic addition of Br_2 to **1** leads to phenyl migration, whereas free-radical addition produces an unrearranged adduct either instead of or in addition to rearranged product.

2. Additions to Diphenylpropene. Solvent Effects in Opening of Three-Membered-Ring Iodonium Ions.—We next turned our attention to 3,3-diphenylpropene (**10**) in which there is less crowding of phenyl groups than in **1**.

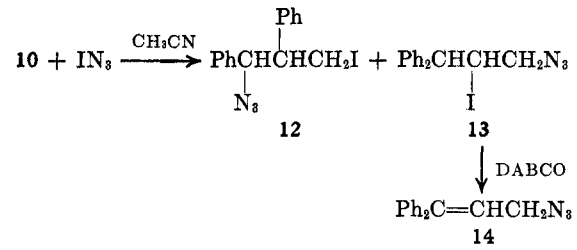
Several routes leading to 3,3-diphenylpropene (**10**) were investigated including the reported method of Walling, *et al.*[7] All led to a mixture of 1,1- and 3,3-diphenylpropene. The most satisfactory method proved to be a Wittig reaction on diphenylacetaldehyde followed by separation of the olefin isomers on $AgNO_3$–alumina. Addition of BrN_3 to **10** under ionic conditions proceeded with phenyl migration to produce in over 80% yield bromoazide **11**, the structure of which was assigned on the basis of its mass spectrum (base peak at *m/e* 104 for $PhCH{=}N^+$) and its low reactivity toward most bases or toward zinc (in analogy to **5** and **7**).

$$Ph_2CCH{=}CH_2\;(\mathbf{10}) + BrN_3 \xrightarrow{CH_3NO_2} PhCCHCH_2Br\;(\mathbf{11})$$
$$\downarrow N_3$$

(7) C. Walling and L. Bollyky, *ibid.*, **28**, 256 (1963).

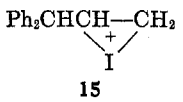
The formation of rearranged product **11** in good yield is indicative of the high propensity for phenyl migration even in the diphenyl system. Since in the monophenyl case (allylbenzene) no rearrangement was observed on IN_3 addition,[8] the presence of a phenyl substituent to stabilize the carbonium ion resulting from phenyl migration (*cf.* **4**) appears essential.

Interestingly, addition of IN_3 to **10** in acetonitrile gave rise to two iodo azide products that were separable by thick layer chromatography. The minor adduct was the expected phenyl rearrangement product **12** as indicated by the base peak in its mass spectrum at *m/e* 104 ($PhCH{=}N^+$). The major product was found to be the nonrearranged adduct **13**. By analogy with **9**,

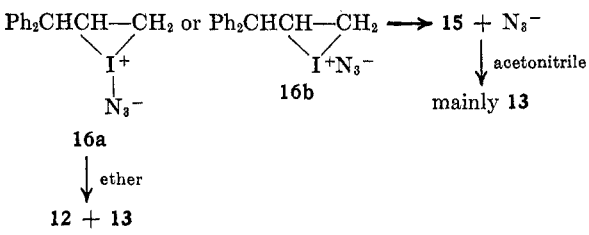


the base peak in the mass spectrum of **13** was at *m/e* 167 (Ph_2CH^+). The regiochemistry of **13** was proven by elimination of HI at 0° by means of 1,5-diazabicyclo-[4.3.0]-5-nonene or of 1,4-diazabicyclo[2.2.2]octane, which furnished the allyl azide **14**. The structure of **14** was obvious from its ir (strong azide absorption at 2112 cm^{-1}), nmr (triplet at τ 3.81 and doublet at τ 6.16), and uv spectrum [λ_{max} 253 nm (ϵ 14,500)].

Opening of the intermediate iodonium ion **15** at the terminal carbon to form **13** has evidently proceeded in a sterically controlled regiospecific manner as was reported for the IN_3 addition to *tert*-butylethylene.[8b]



Since IN_3 additions are generally ionic, the formation of both rearranged and nonrearranged adducts (**12** and **13**) was somewhat surprising. In order to determine whether adduct **13** was the result of a free-radical addition, we attempted to carry out the IN_3 addition in ether. This was possible by generation of IN_3 from silver azide (*caution!*) and ICl in ether. Although the reaction was slow in ether and *ca.* 20% of unreacted olefin **10** was recovered, we were able to obtain adducts **12** and **13** in 33% yield each. These results were not compatible with a free-radical pathway leading to **13**. We interpret the unusual solvent effect in the IN_3 addition to **10** in the following manner. In ether, a solvent of low polarity, the iodonium ion exists as a complex or a tight ion pair of type **16a** or **16b** which can undergo

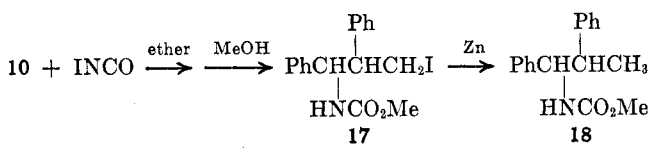


opening of the three-membered ring by phenyl migration to produce **12** or by attack of azide ion to form **13**. In a solvent of higher polarity, such as acetonitrile, dissociation of **16** into N_3^- and **15** takes place more readily and opening of **15** by azide ions competes more effectively with phenyl migration. To lend further support for this view, the IN_3 addition to **10** in ether was carried out in the presence of an excess of tetramethylammonium azide. As expected, the ratio of **13**:**12** increased considerably as shown in Table II.

TABLE II
SOLVENT EFFECTS ON PHENYL MIGRATION IN THE ADDITION OF IN_3 TO **10**

Solvent	Ratio of 13/12
Acetonitrile	6
Ether	1
Ether + $Me_4\overset{+}{N}N_3^-$	24

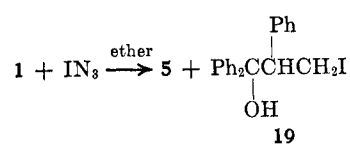
Somewhat similar results were obtained on INCO addition to 3,3-diphenylpropene (**10**) in ether. The resulting isocyanate was not isolated but converted with methanol to a crude carbamate. The latter was difficult to purify and was isolated in variable yield suggesting that it may consist of a mixture of isomers. However, only one pure carbamate product (**17**) could be isolated in 30–40% yield. Its structure was assigned on the basis of its mass spectrum (base peak at *m/e* 164, $PhCH{=}N^+HCO_2Me$) and zinc reduction to methyl *N*-(1,2-diphenyl-1-propyl)carbamate (**18**). The



structure of **18** was evident from its nmr and mass spectrum. The latter had the same characteristic base peak as **17**. The nmr spectrum indicated the presence of a *C*-methyl group as a doublet at τ 8.84 confirming the position of the iodo function in **17**.

In the BrN_3 addition to **10** in CH_3NO_2, the three-membered-ring bromonium ion is more easily equilibrated to a secondary carbonium ion than its analogous iodonium ion **15**;[9] hence, phenyl migration is more facile and only the rearranged product is observed.

The lack of formation of a 1,2 adduct of type **13** in the IN_3 addition to triphenylpropene **1** in acetonitrile is probably due to the higher propensity for phenyl migration in the trityl than in the diphenylmethyl system. When IN_3 was added to **1** in ether, **5** was obtained in 55% yield together with unreacted olefin and other products. Separation by chromatography led to the isolation of the iodohydrin **19** in 20% yield. This com-



pound was unstable and was converted upon standing in CCl_4 into 2,3-diphenylindene. The formation of the

(8) (a) F. W. Fowler, A. Hassner, and L. A. Levy, *J. Amer. Chem. Soc.*, **89**, 2077 (1967); (b) A. Hassner and F. W. Fowler, *J. Org. Chem.*, **32**, 2686 (1968).

(9) A. Hassner, F. Boerwinkle, and A. B. Levy, *J. Amer. Chem. Soc.*, **92**, 4879 (1970).

iodohydrin is probably due to the presence of water from incompletely dried AgN_3.

Experimental Section[10]

Ionic Addition of Bromine Azide to 3,3,3-Triphenylpropene (1).—Following the general procedure for BrN_3 additions in nitromethane,[9] 0.54 g (2 mmol) of triphenylpropene 1 was converted to 0.95 g of crude adduct. The product was placed in a quartz tube on 10 g of Woelm neutral alumina impregnated with 1% zinc silicate–manganese luminescent indicator. The column was eluted with CCl_4 (19 ml) until all the organic material was removed from the column, as judged by observation with a short-wave uv lamp. Removal of the solvent left 0.89 g (100%) of a partially solid product. Recrystallization from hexane gave two crops of crystals: 360 mg, mp 84–87°, and 179 mg, mp 84–92°. Another recrystallization of the first crop gave an analytical sample (prisms) of **7**: mp 86–88°; ir 2112 (N_3) and 633 cm^{-1} (CBr); nmr τ 2.5–3.1 (m, 13), 3.1–3.4 (m, 2), 5.8 (dd, 1, J = 2.2 and 11.2 Hz), 6.0 (dd, 1, J = 2.2 and 10.3 Hz), 6.42 (dd, 1, J = 11.2 and 10.3 Hz); mass spectrum m/e (rel intensity) 51 (10), 77 (43, Ph^+), 104 (20), 180 (100, Ph_2CN^+), 181 (16). A high resolution mass spectrum of **7** indicated that the ions at m/e 180 correspond to the elemental composition, $C_{13}H_{10}N$.

Anal. Calcd for $C_{21}H_{18}BrN_3$: C, 64.29; H, 4.63; N, 10.71. Found: C, 64.67; H, 4.74; N, 10.54.

Recrystallization of the second crop from hexane gave a mixture of **7** as pale yellow prisms, mp 84–87°, and of **3** as a white powdery solid, mp 120–125° (lit.[2] 125–127°). Using micro techniques, 3 mg of crystals of **3** were separated and analyzed: ir 631 cm^{-1} (CBr); uv (95% EtOH) λ_{max} 229 nm (ϵ 30,000), 276 (16,600).

Anal. Calcd for $C_{21}H_{17}Br$: C, 72.21; H, 4.91. Found: C, 72.77; H, 5.17.

Examination of the nmr spectra of the crude product showed, besides the peaks for the bromoazide **7**, a singlet at τ 5.71 (lit.[2] τ 5.59). An approximate integration of the peaks showed the original azide product to consist of 83% 3-azido-2,3,3-triphenylpropyl bromide (**7**), 7% 2,3,3-triphenylallyl bromide (**3**), and 11% 3,3,3-triphenylpropene (**1**).

Treatment of bromoazide **7** with potassium *tert*-butoxide in DMSO by the described procedure[3] afforded triphenylacrolein (**8**) in 55% yield.

Free-Radical Additions of Bromine Azide to 3,3,3-Triphenylpropene (1).—Following the described procedure,[4,9] 197 mg of **1** was stirred with a solution of BrN_3 in pentane (from 3.0 g of bromine) under N_2 for 27 hr in the presence of light and benzoyl peroxide. Work-up gave 248 mg of a solid consisting of 54% **1** and 30% **9**. Separation by preparative thick layer chromatography on silica gave pure adduct **9**: mp 96–100°; ir 2121 cm^{-1} (N_3); mass spectrum m/e (rel intensity) 51 (10), 77 (14), 115 (8), 165 (33), 178 (11), 180 (13), 243 [100, $(Ph_3)C^+$], 244 (19), 282 [3, $M\cdot^+ - (N_2 + H + HBr)$], 284 [9, $M\cdot^+ - (N_2 + Br)$], 363 (2, $M\cdot^+ - N_2$).

Anal. Calcd for $C_{21}H_{18}BrN_3$: C, 64.29; H, 4.63. Found: C, 64.39; H, 4.59.

Addition of Bromine to 3,3,3-Triphenylpropene (1).—Following the described procedure[2], 0.33 g (2.1 mmol) of bromine was added to 0.541 g (2 mmol) of **1** in CCl_4 to give after 48 hr a mixture of **2** and **3** in a ratio of 45:55 as determined by nmr integration.

When the same reaction was carried out in the dark in the presence of O_2 (bubbling O_2 into the CCl_4 for 5 min), the product contained 73% **3** and 11% **2**. In the presence of O_2 and a trace of di-*tert*-butylphenol, 0.886 g of product, mp 115–128°, was obtained which contained 88% **3** as indicated by the integration of the singlet at τ 5.72 *vs.* the aromatic multiplet. One crystallization from hexane–CCl_4 furnished pure allyl bromide **3**: mp 124–125° (lit.[2] 125–127°); mass spectrum m/e (rel intensity) 180 (100, $Ph_2C{=}N^+$).

3,3-Diphenylpropene (10).—Following the procedure of Corey, *et al.*,[11a] for preparation of 1,1-diphenylpropene, a solution of dimethyl sulfinyl anion in DMSO, prepared from 2.16 g (0.09 mol), of NaH and 55 ml of DMSO under N_2, was treated with 32.1 g (0.09 mol) of freshly prepared triphenylmethylphosphonium bromide[11b] in 90 ml of DMSO. After stirring for 25 min, a solution of 19.6 g (0.1 mol) of diphenylacetaldehyde in 30 ml of DMSO was added in one portion. This was stirred for 29 hr at 60°. The product was poured into 265 g of ice water and extracted with five 100-ml portions of Skellysolve B. The combined extracts were washed once with water, dried (Na_2SO_4), and evaporated to give 14.5 g (83%) of an oil. The nmr integration indicated a mixture of 65% 3,3-diphenylpropene, 10% 1,1-diphenylpropene, and 25% diphenylacetaldehyde. Other attempts using different proportions of NaH and $Ph_3P^+CH_3Br^-$ gave similar results. This mixture was taken up in 75 ml of ether and shaken with a solution of 25 g of $NaHSO_3$ in 75 ml of water for 5 min. After washing with three 75-ml portions of water, the product was dried ($MgSO_4$) and evaporated to give 11.9 g (68%) of an oil which was composed of 84% 3,3-diphenylpropene and 16% 1,1-diphenylpropene.

The mixture of isomers obtained above (11.9 g) was chromatographed on 400 g of 10% $AgNO_3$ on alumina. On elution with 1000 ml of hexane and solvent evaporation, 0.3 g of 1,1-diphenylpropene was obtained, mp 42–50° (lit.[11a] 48.5°), as indicated by an nmr doublet at τ 8.37. Elution with 300 ml of cyclohexane gave 1.4 g more of this isomer, mp 42–48°. Removal of 3,3-diphenylpropene from the column required 700 ml of benzene which gave, after rotary evaporation, 7.3 g of 3,3-diphenylpropene of *ca.* 95% isomeric purity. Further purification was easily accomplished by freezing the oil in a Dry Ice–acetone bath and adding 3 vol of pentane. The mixture was swirled in an ice bath until nearly dissolved and then placed in the freezer. Fractional crystallization over a period of 3–5 days gave pure 3,3-diphenylpropene, recovered by filtration through an ice-cooled Büchner funnel. This method of crystallization was applicable only to mixtures of over 90% isomeric purity. The product melted at 14.5–16° on a precooled stage and showed nmr and ir spectra matching those reported for **10**.[7,12]

Ionic Addition of Bromine Azide to 10.—The addition was carried out following the general procedure.[8] From 0.391 g (2.0 mmol) of 3,3-diphenylpropene (**10**) there was obtained 0.624 g (98%) of pale reddish oil, homogeneous by tlc. Both crude and chromatographed samples gave correct analysis. The adduct was inert to zinc–acetic acid, tertiary amines, and potassium *tert*-butoxide in ether suggesting the rearranged structure **11**: ir 2100 cm^{-1} (N_3); nmr (CCl_4) τ 2.8–3.2 (m, 10), 4.3–5.3 (m, 1), 6.1–7.0 (m, 3); mass spectrum m/e (rel intensity) 77 (15), 89 (16), 91 (66), 103 (15), 104 (100%, $PhCH{=}N^+$ and $Ph^+CHCH_2\cdot$), 115 (29), 165 (14), 169 (40), 171 (39), 178 (22), 179 (20), 180 (14), 183 (14), 185 (14), 273 (51, $M - HN_3$), 275 (50).

Anal. Calcd for $C_{15}H_{14}BrN_3$: C, 56.98; H, 4.46. Found: C, 57.14; H, 4.44.

Iodine Azide Addition to 3,3-Diphenylpropene (10) in Acetonitrile.—The addition[8] was carried out using 0.58 g (3 mmol) of **10**. The reaction mixtures were stirred for 19 hr and quenched to give on work-up 1.01 g (93%) of an oil which by nmr was shown to be 94% of adduct **13** and 6% of olefin **10**. Tlc using 2.5% ethyl acetate in hexane gave optimum separation into four fractions: R_f 0.18, 0.23, 0.34, and 0.50 (the last one was identical with diphenylpropene). A part of the product, 0.75 g, was subjected in three portions to preparative thick layer chromatography. Extraction with CH_2Cl_2 and rotary evaporation gave three fractions (total of 0.57 g), each showing strong azide absorption (*ca.* 2100 cm^{-1}) in the ir. The last fraction (3%) also had a strong peak at 1660 cm^{-1} suggesting a vinyl azide structure. The first fraction consisted of 80 mg (14%) of **3-azido-2,3-diphenyl-1-propyl iodide (12)** as an oil: mass spectrum m/e (rel intensity) 51 (13), 77 (57, Ph^+), 78 (16), 91 (19), 103 (17), 104 (100, $PhCH{=}N^+$), 105 (23), 165 (0), 167 (13).

Anal. Calcd for $C_{15}H_{14}IN_3$: C, 49.60; H, 3.89; I, 34.94. Found: C, 49.25; H, 3.93; I, 34.41.

The second fraction (0.47 g, 83%) consisted of **1-azido-3,3-**

(10) All solvents used were distilled. Melting points were determined on a Fisher block and are uncorrected. Infrared spectra were obtained using *ca.* 3% w/v solution in CCl_4 with a 0.5-mm KBr solution cell unless otherwise noted on a Perkin-Elmer 457 instrument. Nmr spectra were obtained on a Varian A-60 or A-60A spectrometer with TMS as an internal standard, using approximately a 20% w/v solution in $CDCl_3$. Uv spectra were recorded on a Cary 14 spectrometer. Mass spectra were obtained at 70 eV on a Varian MAT CH5 mass spectrograph. Elemental analyses were performed by Galbraith Laboratories, Knoxville, Tenn. Thin layer chromatographs were carried out on silica gel PF_{254} precoated plates or silica gel PF_{254} 2-mm coated plates for preparative layers.

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diphenyl-2-propyl iodide (13) which slowly solidified in the freezer, mp 47–60°. Chromatography of a small amount on 15 g of Woelm neutral alumina gave, on elution with benzene, a pure solid in the first fractions: 0.10 g; mp 56–58°; mass spectrum *m/e* (rel intensity) 51 (26), 77 (74), 78 (23), 91 (60), 103 (38), 104 (57), 105 (33), 115 (33), 117 (20), 130 (18), 152 (21), 165 (60), 166 (21), 167 (100, Ph_2CH^+), 178 (31), 179 (40), 180 (60), 181 (30), 193 (31), 208 (30).

Anal. Calcd for $C_{15}H_{14}IN_3$: C, 49.60; H, 3.88. Found: C, 49.86; H, 3.88.

3-Azido-1,1-diphenylpropene (14).—Elimination of HI from 0.18 g of 13 following the procedure of Hassner and Fowler[8] using 0.13 g of 1,5-diazobicyclo[4.3.0]-5-nonene (DBN) in acetone for 18 hr gave 0.127 g (100%) of 14 (82% pure by nmr integration). This was subjected to preparative thick layer chromatography using 2.5% ethyl acetate in hexane as an eluent to give 0.049 mg (42%) of the pure allylic azide 14 which solidified to give an analytical sample, mp 30–31°. Use of [2.2.2]-diazabicyclooctane in the same procedure gave a 53% yield of 14: ir 2112 (N_3) and 1599 cm^{-1} (C=C); nmr τ 2.4–2.9 (m, 10), 3.81 (t, 1, J = 7.5 Hz), 6.16 (d, 2, J = 7.5 Hz); uv (95% EtOH) λ_{max} 230 nm (ϵ 14,500), 253 (14,500).

Anal. Calcd for $C_{15}H_{13}N_3$: C, 76.57; H, 5.57; N, 17.86. Found: C, 76.34; H, 5.42; N, 17.65.

General Procedure for Iodine Azide Addition in Ether.—A predried 50-ml three-necked flask fitted with a mechanical stirrer and gas outlet was connected directly to an apparatus for distilling ether from $LiAlH_4$. The flask and distillation apparatus were flushed with a stream of dry nitrogen and *ca.* 10 ml of ether was distilled into the flask. Silver azide was freshly prepared by mixing 0.68 g (4.04 mmol) of $AgNO_3$ in 20 ml of distilled water and 0.260 g (4.00 mmol) of NaN_3 in 4 ml of distilled water in an ice bath. The azide was filtered through a coarse sintered glass funnel fitted with a piece of glass fiber filter paper and was quickly washed with three 10-ml portions of distilled water and five 10-ml portions of anhydrous ether. The cake of AgN_3 was transferred immediately into the reaction flask using a Nalgene powder funnel. (*Caution!* Dry silver azide is extremely shock sensitive.) The flask was covered with a serum stopper and connected with a reflux condenser–drying tube. The mixture was cooled to −80° in a Dry Ice–acetone bath and stirred during the rapid addition of 0.488 g (3 mmol) of ICl. The flask was covered with foil and an ice bath was substituted for cooling. The solution was stirred an additional 10–15 min, 2 mmol of the olefin was added, and the ice bath was removed. After being stirred for 15–24 hr more, the reaction mixture was forced through Celite 545 into a saturated $NaHSO_3$ solution. The same work-up was used as described for IN_3 additions in acetonitrile.[8] Deviations are noted for specific compounds.

Addition of IN_3 to 3,3-Diphenylpropene (10) **in Ether.**—Using the general procedure, 0.433 g (2.03 mmol) of 3,3-diphenylpropene (10) was converted into 0.624 g (88%) of adduct. Nmr spectra showed that *ca.* 20% of the starting olefin was left unreacted. Elution of 0.48 g of the product in two portions gave 0.42 g of recovered product consisting of five fractions. The first fraction 72 mg (17%) was identified as 3,3-diphenylpropene (10) by ir. Recovery of the next two fractions gave 133 mg of 12 (32%) and 137 mg of 13 (33%). Ir and mass spectra for these compounds were identical with those given above. The fourth fraction, 12 mg (3%), appeared to be a vinyl azide (ir 2100 and 1660 cm^{-1}) and the fifth, 69 mg (15%), gave only a weak azide peak in the ir. Further indentification of these compounds was not attempted.

Addition of IN_3 to 3,3,3-Triphenylpropene (1) **in Ether.**—From 0.54 g (2.00 mmol) of 3,3,3-triphenylpropene (1) was obtained 0.859 g (98%) of an oil. Elution of two 0.24-g portions of the product on preparative layer chromatograms using 5% ethyl acetate in hexane gave five fractions (0.37-g total). Unreacted 1 (24 mg, 7% of recovered material) was found to be in the first fraction. The ir of the second (60 mg, 16%) and fourth (8 mg, 2%) fractions failed to show azide absorptions and further identification was not attempted. The third fraction (205 mg, 55%) proved to be 3-azido-2,3,3-triphenyl-1-propyl iodide (5) by comparison of ir and nmr spectra.

The fifth fraction gave 71 mg (20%) of a brown-white solid: mp 120–125° dec; nmr (CCl_4) τ 2.4–3.2 (m, 15), 5.83 (2 d, 1), 6.43 (m, 2), 7.5 (s, 1). Cooling of the nmr sample in CCl_4 after *ca.* 2 hr at 25° gave 19 as a white crystalline solid, mp 99–101° dec.

Anal. Calcd for $C_{21}H_{19}IO$: C, 60.88; H, 4.62. Found: C, 60.62; H, 4.54.

When a solution of 19 in CCl_4 was allowed to stand for 24 hr, evaporation yielded crude 2,3-diphenylindene, mp 100–105° (lit. 110–112°), identified by ir and nmr comparison with an authentic sample.[2,3]

Methyl *N*-(3-Iodo-1,2-diphenyl-1-propyl)carbamate (17).—Addition of iodine isocyanate[13] to diphenylpropene 10 and treatment with methanol gave the crude 1,3-iodo carbamate 17 in variable yields (55–80%). Recrystallization from methanol gave an analytical sample: mp 167–169°; white needles; ir 3450 (NH), 1710 cm^{-1} (C=O); nmr τ 2.7–3.2 (m, 10), 4.7–5.2 (m, 2), 6.43 (s, 3), 6.5–7.0 (m, 2); mass spectrum *m/e* (rel intensity) 42 (19), 43 (12), 57 (13), 77 (14), 78 (10), 104 (33), 121 (11), 132 (10), 149 (13), 164 (100, $PhCH{=}N^+HCO_2CH_3$), 165 (12).

Anal. Calcd for $C_{17}H_{18}INO_2$: C, 51.62; H, 4.59; N, 3.54. Found: C, 51.29; H, 4.41; N, 3.54.

Methyl *N*-(1,2-Diphenyl-1-propyl)carbamate (18).—Reduction of 17 (0.190 g, 0.48 mmol) in 0.75 ml of acetic acid was carried out with 0.1 g of freshly activated zinc[14] at 70°. After stirring magnetically for 2 hr at 70°, the mixture was filtered, neutralized with solid Na_2CO_3, and extracted with ether. Evaporation gave a white powdery solid, mp 120–133°, yield 0.139 g (100%). Recrystallization from methanol gave 49 mg (38%) of an analytical sample: mp 142–143°; nmr τ 2.75 (s, 10), 4.9–5.4 (m, 1), 6.50 (s, 3), 6.99 (p, 1), 8.84 (d, 3); mass spectrum *m/e* (rel intensity) 42 (35), 59 (10), 77 (12), 104 (10), 105 (12), 121 (16), 164 (100, $PhCH{=}N^+HCO_2CH_3$).

Anal. Calcd for $C_{17}H_{19}NO_2$: C, 75.81; H, 7.11. Found: C, 75.99; H, 6.98.

Registry No.—**1**, 3282-07-3; **3**, 16536-01-9; **7**, 29182-53-4; **9**, 29182-54-5; **10**, 3542-14-1; **11**, 29182-56-7; **12**, 29182-57-8; **13**, 29182-58-9; **14**, 29182-59-0; **17**, 29182-60-3; **18**, 29182-61-4; **19**, 29182-62-5; bromine azide, 13973-87-0; iodine azide, 14696-82-3.

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