

were done. Generally, eight to ten tubes were prepared for each run. The tubes were placed in a metal rack which was then immersed in the thermostated Ucon oil bath (each tube was immersed up to 13 cm). It usually took 1.5–2.5 min for the temperature of the solution to reach equilibrium with the bath temperature. This was taken as the zero time of the reaction; one tube was withdrawn and immersed immediately in a Dry Ice-acetone bath as the zero time. The other tubes were withdrawn at suitable time intervals in the same way. The last tube was usually removed after about three half-lives of the reaction. The tubes were stored in Dry Ice until the ir analyses could be effected.

Analyses of the Kinetic Runs by Infrared Spectroscopy and Treatment of the Data.—The rate of thermal decomposition was followed by measuring the decrease in absorbance of the selected carbonyl band, Table IV, using a Perkin-Elmer Model 621

TABLE IV

Compd	Solvent	Band used, cm^{-1}
Di- <i>t</i> -butyl dithioltricarboxylate	Chlorobenzene	1840
Di- <i>t</i> -butyl dithioltricarboxylate	Decalin	1837
Di- <i>t</i> -butyl dithiolbicarbonate	Decalin	1773
Di- <i>t</i> -butyl tricarbonate	Chlorobenzene	1870
Di- <i>t</i> -butyl tricarbonate	Decalin	1805
Di- <i>t</i> -butyl dicarbonate	Decalin	1775

infrared spectrometer²⁰ and KBr cells of 0.5-mm thickness. Beer's law was shown to be followed in all cases where the initial

(20) Cf. P. D. Bartlett and R. R. Hiatt, *J. Amer. Chem. Soc.*, **80**, 1398 (1958).

concentration of the tricarbonate or dicarbonate was less than 4×10^{-2} mol.

The spectrum was scanned two to three times in the region of 1950–1650 cm^{-1} . The same procedure was used for all the kinetic runs. Transmittance (T_0 and T_{100}) were adjusted at the carbonyl maximum of the band measured when both cells were filled with pure solvent. To avoid the possibility of setting the pen against the mechanical stop, zero transmittance was set at 0–5% and 100% was set at 95–100%. The true per cent transmittance, T_x , of a sample was thus calculated from the observed transmittance, T_{obsd} , $T_x = (T_{\text{obsd}} - T_0)/(T_{100} - T_0)$. Each time the sample cell was cleaned with spectroscopic grade carbon tetrachloride and dried under a stream of air, and rinsed two or three times with the sample solution which was warmed to room temperature before analysis.

Generally in the region of 20–80% transmittance, the transmittance could be determined with an accuracy of $\pm 0.3\%$. Therefore the tricarbonate and dicarbonate solutions were made up at (or uniformly diluted to) such a concentration that the zero time would be around 20–30% and thus two to three half-lives transmittance would be around 80%. From the per cent transmittance, the optical density at time t was obtained, and first-order rate constants were determined from the slope of the first-order plots of $\log OD_t/OD_0$ against time. The activation parameters were calculated from the Eyring equation in the usual way.²¹

The enthalpy of activation, ΔH^\ddagger , was obtained at 100° from the Arrhenius energy of activation which was determined from the slope through the points on a plot of $\log k$ against $1/T$. The entropy of activation, ΔS^\ddagger , was calculated at 100° by substituting the known value of ΔH^\ddagger into the equation.

Registry No.—4a, 22085-39-8; 4b, 24424-95-1.

(21) A. A. Frost and R. G. Pearson, "Kinetics and Mechanism," Wiley, New York, N. Y., 1961, p 98.

Phenyl Migration in Pseudohalogen Additions to 3,3,3-Triphenylpropene¹

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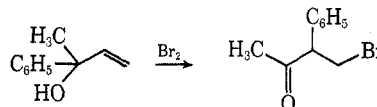
Received April 3, 1970

Addition of iodine azide (IN_3) to tritylethylene (1), unlike to *t*-butylethylene, leads to complete rearrangement producing 3-azido-2,3,3-triphenyl-1-propyl iodide (2) in 99% yield. Treatment of 2 with potassium *t*-butoxide gave triphenylacrolein. Under milder conditions it was possible to isolate an intermediate allylic azide. A rearranged product was also noted on iodine isocyanate addition to 1. Similarly, benzonorbornadiene gave a 1,3 adduct resulting from a Wagner-Meerwein phenyl migration and methylenenorbornene produced a rearranged IN_3 adduct.

Though electrophilic addition of halogens to terpene olefins often leads to rearrangement of the carbon skeleton,² there are reported only few instances of alkyl migration occurring during halogen additions to acyclic olefins. A favorable case such as *t*-butylethylene, for example, which gives 60% methyl migration in HCl addition, renders no rearranged products when Cl_2 , Br_2 , or IN_3 is added to it under ionic conditions.³ The first example of rearrangement in an acyclic system appears to be the Cl_2 addition to *trans*-di-*t*-butylethylene.⁴

Many more examples exist for phenyl migration. Although addition of HBr in acetic acid to allylbenzene gives only the normal adduct in 92% yield,⁵ the presence

of two of three allylic phenyl groups or of a hydroxy group augments rearrangement by stabilizing the carbonium ion resulting from phenyl migration.^{6,7} Such an example is shown below for bromine addition to 2-phenyl-3-buten-2-ol.



Recent studies on the reaction of olefins with iodine azide (IN_3) revealed that such additions occur with a remarkably high degree of stereo- and regioselectivity,⁸ suggesting a three-membered ring iodonium ion intermediate. Thus *n*-butylethylene adds IN_3 to yield 2-

(1) Stereochemistry. LIV. For the previous paper in this series, see A. Hassner, F. P. Boerwinkle, and A. B. Levy, *J. Amer. Chem. Soc.*, **92**, 4879 (1970).

(2) See, for instance, H. Kwart, *ibid.*, **75**, 5942 (1953); L. Kaplan, H. Kwart, and P. von R. Schleyer, *ibid.*, **82**, 2341 (1960).

(3) (a) G. C. Ecker, N. E. Cook, and F. C. Whitmore, *ibid.*, **72**, 1511 (1950); (b) W. H. Puterbaugh and M. S. Newman, *ibid.*, **79**, 3469 (1957); (c) A. Hassner and F. W. Fowler, *J. Org. Chem.*, **32**, 2686 (1968).

(4) W. H. Puterbaugh and M. S. Newman, *ibid.*, **81**, 1611 (1959).

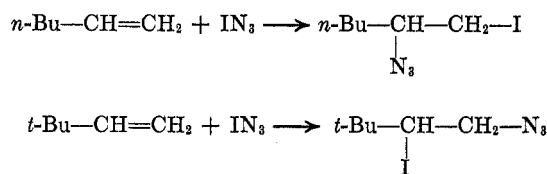
(5) H. E. Carter, *J. Biol. Chem.*, **108**, 619 (1935).

(6) I. V. Bodrikov, V. R. Karwashov, and T. I. Temikova, *Russ. J. Org. Chem.*, **3**, 1640 (1967).

(7) While this work was in progress the addition of bromine to 1 was reported by R. O. C. Norman and C. B. Thomas, *J. Chem. Soc. B*, 598 (1967).

(8) *Regio* is used to describe directional effects in bond making and breaking: A. Hassner, *J. Org. Chem.*, **32**, 2684 (1968).

azidohexyl iodide, whereas *t*-butylethylene gives a non-rearranged product of opposite regiochemistry.^{3c}



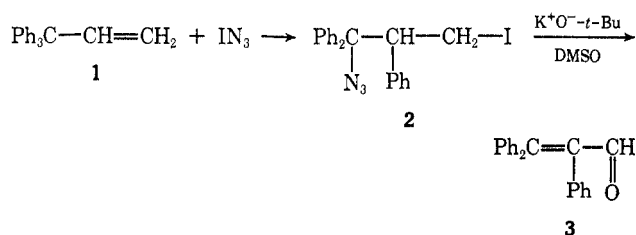
The greater stability of a three-membered-ring iodonium *vs.* bromonium ion was suggested by the stereospecific anti addition of IN_3 to *cis*- β -deuteriostyrene as contrasted to the stereorandom addition of BrN_3 to this olefin.^{9a}

It was therefore of interest to determine whether phenyl migration will occur with opening of an iodonium ion. The foregoing considerations prompted us to investigate the behavior of tritylethylene (3,3,3-triphenylpropene, 1) toward IN_3 and INCO .

Results and Discussion

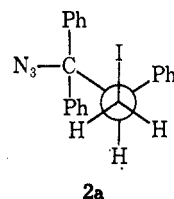
When 3,3,3-triphenylpropene (1) was added to a solution of IN_3 in acetonitrile, the 1,3 adduct, 3-azido-2,3,3-triphenyl-1-propyl iodide (2), was obtained in 99% yield. The evidence for this structure is as follows. The mass spectrum of 2 shows a base peak at *m/e* 180 ($\text{Ph}_2\text{C}=\text{N}^+$) and a smaller peak at 208 ($\text{Ph}_2\text{C}^+-\text{N}_3$), whereas the 1,2-dibromide of 1 has its base peak at 243 (Ph_3C^+). Though phenyl migrations can occur in the mass spectrometer, such rearrangements should not account for the base peak. The nmr spectrum of adduct 2 shows aromatic peak areas in a ratio of 13:2, the two low field protons presumably belonging to the migrated phenyl group. This phenomenon also has been noted by Norman, *et al.*,⁷ for the rearranged 1,3-bromomethoxide formed by the addition of Br_2 to 1 in methanol.

Finally, treatment of 2 with potassium *t*-butoxide in ether or with tertiary amines in acetone, a general reaction for 1,2-iodoalkyl azides,^{3c} failed to cause HI elimination. When the solvent was dimethyl sulfoxide, however, an immediate color change was observed and nitrogen gas was evolved. The product formed in 82% yield, proved to be triphenylacrolein (3), identified by

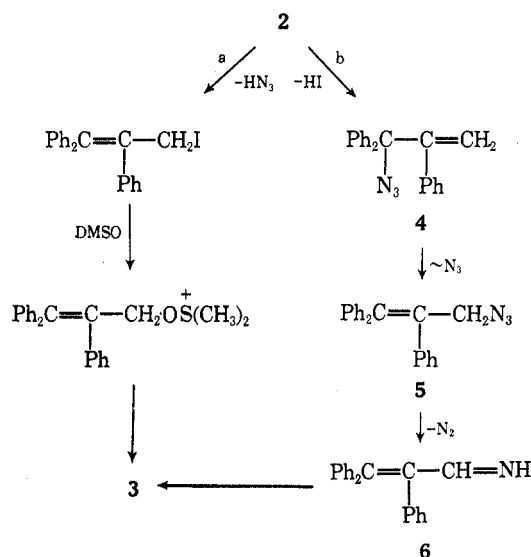


its nmr spectrum, melting point, and 2,4-dinitrophenylhydrazone derivative. The low reactivity of alkyl iodide 2 toward base can be attributed either to the high degree of steric interaction in the conformer 2a

leading to anti elimination of HI or to steric hindrance in the approach of *t*-butoxide to 2.

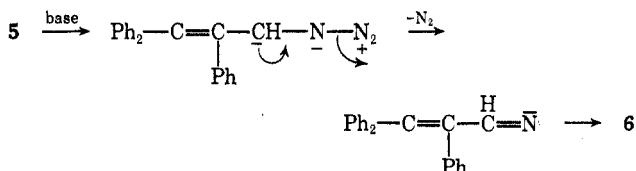


Two plausible pathways are suggested below for the transformation of 2 to 3.

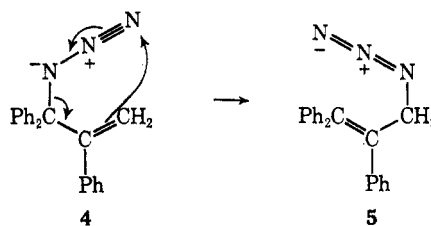


Differentiation between these paths became possible by carrying out the reaction in ether-DMSO (82:18) at 0°, in which case intermediate 5 was isolated.^{9b} This azide, a stable white solid, was identified by nmr which shows three singlets in the aromatic region (5:5:5 protons) and one at τ 5.88 (two protons). Its uv spectrum indicated extensive conjugation at 276 nm (ϵ 16,700). By comparison, α -methyl- β -phenylstilbene has a maximum at 275 nm (ϵ 10,000). Further proof for structure 5 was furnished by its synthesis from allyl bromide 10 with NaN_3 .

Treatment of 5 with potassium *t*-butoxide in DMSO gave 3 and 1 equiv of N_2 was collected during the reaction. This transformation which requires the presence of base, apparently involves proton abstraction from 5 and loss of N_2 to yield the anion of 6. Hydrolysis of the imine 6 furnishes 3.



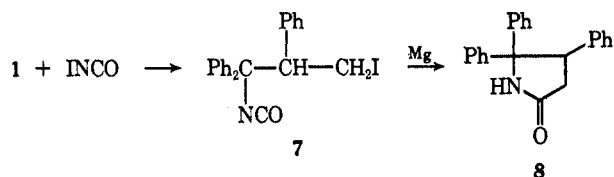
The other interesting feature in the conversion of 2 to 3 is the rearrangement of allyl azide 4 to 5 which prob-



(9) (a) See Hassner, *et al.*,¹ and references cited. (b) The well-known conversion of alkyl halides to aldehydes by means of DMSO (path a) [N. Kornblum, W. J. Jones, and G. J. Anderson, *J. Amer. Chem. Soc.*, **81**, 4113 (1959)], is not followed in this case and instead dehydroiodination is being facilitated by the polar solvent.

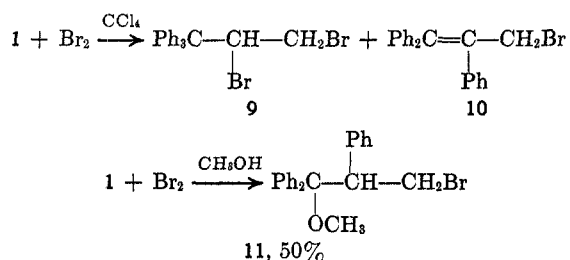
ably involves a concerted migration of the azide function leading to the more substituted olefin.¹⁰

Addition of iodine isocyanate to triphenylpropene **1** in ether led to an adduct in 60–75% yield, to which structure **7** is assigned by analogy with **2** and on the basis that, as a hindered tertiary isocyanate, **7** showed a low reactivity toward methanol in the presence of LiOCH₃.¹¹



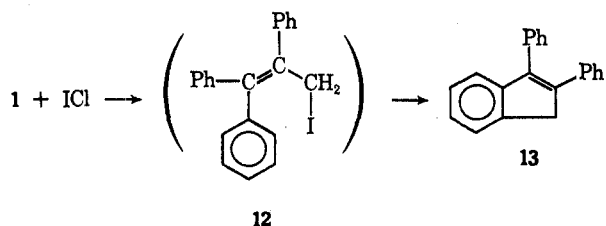
Treatment of **7** with magnesium in ether, after initiation of the Grignard reaction with methyl iodide, furnished lactam **8**. The γ -lactam structure, rather than a β -lactam which could have arisen from intramolecular cyclization of a 1,2-INCO adduct, was apparent from the characteristic carbonyl stretching frequency at 1695 cm⁻¹.

It is useful to contrast the addition of the nitrogen containing pseudohalogens IN₃ and INCO to that of Br₂. In an extensive investigation of **1** and related systems, Norman and coworkers⁷ found that bromine addition to **1** in CCl₄ led to the 1,2 adduct **9** and the allylic bromide **10** in a ratio of 4:6. The allylic bromide presumably arose from dehydrobromination of a



primarily formed 1,3-dibromo adduct. In the presence of methanol a rearranged 1,3 adduct **11** was obtained in 50% yield.

It was therefore of interest to determine which course the addition of ICl to triphenylpropene **1** would take. The reaction proceeded readily in either acetonitrile or ether to produce 2,3-diphenylindene (**13**), which most likely resulted from the allyl iodide **12** by solvolytic



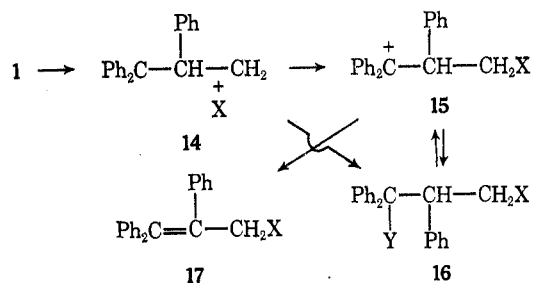
ring closure. Indene **13** was also formed in the attempted Prevost reaction (I₂-AgOAc) on **1**.¹²

(10) A. Gagneux, S. Winstein, and W. G. Yound, *J. Amer. Chem. Soc.*, **82**, 5956 (1960).

(11) A. Hassner, M. E. Lorber, and C. Heathcock, *J. Org. Chem.*, **32**, 540 (1967).

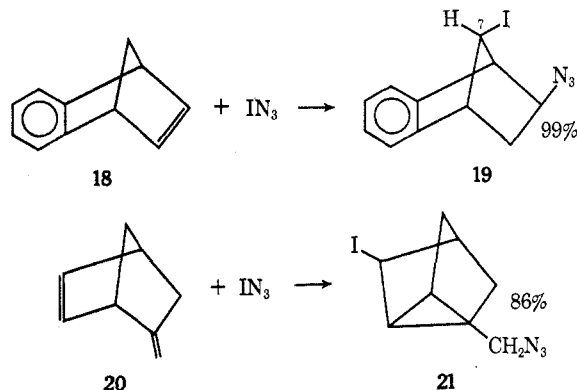
(12) R. O. C. Norman and C. B. Thomas, *J. Chem. Soc. B*, 604 (1967).

It is clear that in the various additions to triphenylpropene **1**, phenyl migration leads to opening of the halonium ion **14**. This can occur either with formation of a carbonium ion **15** or of a bridged phenonium ion, or in a concerted manner with the nucleophile Y⁻ forming a bond as the phenyl group migrates. When Y⁻ is azide or isocyanate ion the adduct **16** is formed irreversibly whereas in most other cases olefin **17** is formed



either directly from **15** or after an equilibrium between **15** and **16** has been established. Opening of the three-membered-ring iodonium ion by phenyl migration is enhanced by the relief of steric crowding of the three phenyl groups and stabilization of a full or incipient positive charge in the transition state by two phenyl groups.

Further examples of rearrangements during IN₃ addition are provided by benzonorbornadiene (**18**) and methylenenorbornene (**20**). The 1,3 adduct **19**, formed in quantitative yield, shows a quintet at τ 5.96 (*syn* H at C-7) diagnostic of an *exo*-5,*anti*-7-dihalobenzo-norbornene system.¹³ The formation of the *exo* isomer **19** suggests a concerted opening of an initially formed



three-membered-ring iodonium ion or involvement of a stabilized nonclassical carbonium ion. The product of IN₃ addition to **20** was an oil that readily decomposed at room temperature. It showed an (M - 127)⁺ instead of an M⁺ peak in its mass spectrum and in the nmr singlets at τ 6.1 (CH-I) and 6.53 (CH₂-N₃) and a multiplet at 7.8–9.1 (integrating for 7 H), consistent with structure **21** or with a regioisomeric nortricyclene. Structure **21** is favored by analogy with the INCO adduct of **20**.¹⁴

(13) S. J. Cristol and G. W. Nachtigall, *J. Org. Chem.*, **32**, 3738 (1967).

(14) A. Hassner, R. P. Hoblitt, C. Heathcock, J. E. Kropp, and M. E. Lorber, *J. Amer. Chem. Soc.*, **92**, 1326 (1970).

Experimental Section¹⁵

3,3,3-Triphenylpropene (1).—This compound was prepared from β,β,β -triphenylpropionic acid by modification of reported procedures.¹⁶ A mixture of 160 ml of *t*-butyl alcohol and 16.5 g (0.422 mol, 4.6 equiv of 2 *N* base) of potassium was heated cautiously under reflux and 35.5 g (0.092 mol) of finely ground 3,3,3-triphenyl-1-propyl iodide (mp 174–177°) was added. The heterogeneous mixture was stirred at reflux for 4.5 days (until the melting point of the solid obtained from work-up of aliquots was 74–78°), and quenched in 300 ml of ice water. Three benzene extracts were combined and washed with water until neutral. After drying (MgSO₄), evaporation gave 24.0 g (93%) of the crude solid, mp 74–80°. Recrystallized from methanol it furnished 21.5 g (90%) of pure 3,3,3-triphenylpropene (1), mp 80–81° (lit.^{16a} 78–78.8°). The nmr and ir spectra were consistent with those reported.⁷

General Procedure for Iodine Azide Additions.—Using a modification of the reported procedure,¹⁷ a 100-ml three-necked round-bottom flask fitted with a reflux condenser, drying tube, and a mechanical stirrer was predried and charged with 2.60 g (40 mmol) of sodium azide and 30 ml of acetonitrile. The flask was covered with foil and stirred in an ice bath during the slow addition of 4.88 g (30 mmol) iodine monochloride using a weighed 2-ml syringe with a Luer-Lok fitting. The mixture was stirred 10–15 min, 20 mmol of the olefin was added, and the ice bath was removed. After stirring for 18–26 hr, the solution was forced with air through Celite 545 in a coarse sintered glass funnel into 50-ml of saturated (50% w/v) sodium bisulfite solution in a 125-ml separatory funnel. Addition of 25 ml of ether and shaking gave a clear ethereal layer which was forced through magnesium sulfate into a tared flask and the solvent removed by rotary evaporation. The adduct was usually obtained as a slightly orange oil.

3-Azido-2,3,3-triphenyl-1-propyl Iodide (2).—Using the general procedure the adduct of 1 was obtained in 99% yield (8.44 g). The oily pale orange adduct solidified on exposure to a stream of air overnight, mp 91–100°. Recrystallization from methanol gave pale yellow crystals: mp 104–106°; ir (neat oil) 2105 (N₃, s), 580 cm⁻¹ (C–I, m); nmr τ 6.69 (dd, 1, *J* = 10 and 11.5 Hz), 6.16 (dd, 1, *J* = 2 and 10 Hz), 5.81 (dd, 1, *J* = 2 and 11.5 Hz), 3–3.4 (m, 2), 2.5–3 (m, 13) (the crude adduct and the analytical sample gave identical nmr spectra); mass spectrum *m/e* (rel intensity) 51 (13), 77 (44, Ph⁺), 78 (12), 104 (35, Ph–C⁺H–CH₂), 180 (100, Ph₂C=N⁺), 181 (15), 208 (20, Ph₂C–N₃⁺). Anal. Calcd for C₂₁H₁₈IN₃: C, 57.41; H, 4.13. Found: C, 57.53; H, 4.15.

Triphenylacrolein (3) from Iodo Azide (2).—To a solution of 0.80 g (1.8 mmol) of the adduct 2 in 12 ml of DMSO was added 13.3 ml of 0.5 *N* potassium *t*-butoxide in DMSO¹⁸ (6.6 mmol, 3.7 equiv of base) with magnetic stirring. An immediate red-black color and nitrogen evolution were observed. After 23 hr the mixture was quenched by pouring into 80 ml of ice water and the resulting emulsion was extracted with three 30-ml portions of benzene. The combined extracts were washed, dried (MgSO₄), and chromatographed on alumina to give 0.38 g (82%) of crude 3, mp 167–182°. Two recrystallizations from methanol furnished a pure sample of triphenylacrolein, mp 180–183° (lit.¹⁹ 177°), which gave a red 2,4-dinitrophenylhydrazone: mp 232–240° (lit.¹⁸ 223–224°); ir (neat oil) 2857, 2755 (–CHO), 1667 (C=O, s), and 1636 cm⁻¹ (C=C, s); nmr τ 0.26 (s, 1, CHO), 2.64 (m, 5), 2.86 (m, 10). Anal. Calcd for C₂₁H₁₆O: C, 88.70; H, 5.67. Found: C, 88.58; H, 5.80.

(15) All solvents used were distilled. Melting points were determined on a Fisher block and are uncorrected. Infrared spectra were obtained using ~3% w/v solution in CCl₄ with 0.5-mm KBr solution cells 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 CDCl₃ unless otherwise noted. Uv spectra were recorded on a Cary 14 spectrometer. Mass spectra were obtained at 70 eV on a Varian MAT CH5 mass spectrometer. Elemental analyses were performed by Chemalytics, Inc., Tempe, Ariz., or Galbraith Laboratories, Knoxville, Tenn. Thin layer chromatographs were carried out on silica gel F₂₅₄ precoated plates or silica gel PF₂₅₄ 2-mm coated plates for preparative layers.

(16) (a) F. J. Piehl and W. G. Brown, *J. Amer. Chem. Soc.*, **75**, 5026 (1953); (b) W. D. McPhee and E. G. Linstrom, *ibid.*, **65**, 2177 (1943).

(17) F. W. Fowler, A. Hassner, and L. A. Levy, *J. Amer. Chem. Soc.*, **89**, 2077 (1967).

(18) F. C. Chang and N. F. Wood, *Steroids*, **4**, 55 (1964).

(19) G. E. Moussa, *J. Appl. Chem.*, **12**, 385 (1962).

2,3,3-Triphenylallyl Azide (5).—Iodo azide 2 (0.33 g, 0.75 mmol) was taken up in 7 ml of dry ether and cooled in an ice bath with magnetic stirring. To the cold solution was added dropwise 1.50 ml of 0.5 *N* *t*-BuOK in DMSO (0.75 mmol). A color change to rust red was observed but no gas evolution was detected. After stirring for 1.5 hr, the reaction mixture was poured into 50 ml of ice water and extracted with ether. The dried ether extract was diluted with 10 ml of CCl₄ and evaporated to a volume of ~5 ml to remove the ether. Two more 10-ml portions of CCl₄ were added and the process was repeated. Nmr integration of the singlet at τ 5.88 versus aromatic peaks indicated the allylic azide in 84% purity but no triphenylacrolein was detectable. The product was inert to DMSO at 25° for 10 hr. Crystallization of the allylic azide from ethanol provided an analytical sample: mp 69–71°; ir 2095 cm⁻¹ (N₃); nmr (CCl₄) τ 2.71 (s, 5), 2.75 (s, 5), 3.04 (s, 5), 5.88 (s, 2); uv max (95% EtOH) 229 nm (ϵ 30,000), 276.5 (16,700).

Anal. Calcd for C₂₁H₁₇N₃: C, 81.00; H, 5.50. Found: C, 81.16; H, 5.69.

Treatment of allyl azide 5 with potassium *t*-butoxide in DMSO under conditions of formation of 3 from 2 led to isolation of triphenylacrolein 3 in 80% yield and evolution of N₂ in 95% yield.

Heating of allyl azide 10⁷ with NaN₃ in acetone for 4 hr led to formation of 5 in 80% yield.

3-Isocyanato-2,3,3-triphenyl-1-propyl Iodide (7).—Addition of iodine isocyanate to 5.24 g of 1 (4 hr at –25°) followed by treatment with methanol–lithium methoxide¹¹ gave, after quenching in water and ether extraction, a mixture of white solid and liquid. Filtration gave 1.45 g (17%) of the 1,3 adduct, mp 145–150°. The liquid filtrate still showed a strong isocyanate peak at 2275 cm⁻¹ and only a weak carbonyl absorption at 1700 cm⁻¹. When the methanol treatment was omitted the isocyanate 7 was recovered in up to 70% yield. Recrystallization from 40% ether in pentane at 0° gave an analytical sample: mp 152–155°; ir 2275 (NCO) and 578 cm⁻¹ (C–I, s); nmr τ 6.46 (dd, 1, *J* = 10 and 11 Hz), 6.0 (dd, 1, *J* = 2.5 and 10 Hz), 5.8 (dd, 1, *J* = 2.5 and 11 Hz); *m/e* (rel intensity), 104 (25), 165 (10), 180 (10, Ph₂C=N⁺), 208 (100, Ph₂C⁺–NCO).

Anal. Calcd for C₂₂H₁₈NOI: C, 60.14; H, 4.13. Found: C, 60.26; H, 4.25.

3,4,4-Triphenyl- δ -lactam (8).—Magnesium turnings (0.115 g, 4.73 g-atoms) and 0.344 g (0.78 mmol) of the 1,3 adduct 7 were added to a predried flask under N₂ and 30 ml of ether (distilled directly from LiAlH₄) was added. Attempts to initiate Grignard reagent formation failed until 3 drops (~0.4 mmol) of methyl iodide was added resulting in a color change and formation of a pasty precipitate. After stirring for 3 hr, the mixture was quenched with 0.75 ml of saturated NH₄Cl, and then with 50 ml of H₂O and extracted with ether. The ethereal layer furnished 0.244 g (100%) of a yellow solid, mp 158–174°. Two recrystallizations from CCl₄ gave an analytical sample, mp 183–184°. This compound analyzed as a monocarbon tetrachloride solvate: mass spectrum *m/e* (rel intensity) 82 (24, CCl₃⁺), 84 (17, CCl₂⁺), 117 (100, CCl₃⁺), 119 (93, CCl₃⁺), 121 (32, CCl₃⁺), 196 (44), 197 (63), 198 (98, M⁺ – NH), 199 (17), 313 (3, M⁺); ir 1694 cm⁻¹ (C=O) and 3435 cm⁻¹ (N–H); nmr (CCl₄) τ 2.2–3.4 (m, 15), 5.46 (t, 1, *J* = 8 Hz), 7.25 (d, 2, *J* = 8).

Anal. Calcd for C₂₂H₁₈NO·CCl₄: C, 59.13; H, 4.10; N, 3.00. Found: C, 59.43; H, 4.09; N, 3.02.

ICl Addition to 1.—Iodine monochloride (2.44 g, 15 mmol) was added slowly to 10 ml of ether with stirring at 0° followed by 2.44 g (15 mmol) of 3,3,3-triphenylpropene and 3 ml of ether. After 24 hr of stirring at 25°, the solution was worked up as in the case of IN₃ additions to give 2.81 g (105%) of crude yellow 2,3-diphenylindene, mp 94–101°. This compound became red-brown at ambient temperatures and gave a positive Beilstein test. The nmr spectrum of the crude products showed singlets at τ 5.62, 5.77, and 6.20 integrating to 7, 14, and 68% of the total aromatic peak (14 H), respectively. One of the singlets (probably τ 5.77) may correspond to the unstable 2,3,3-triphenylallyl iodide. Recrystallization from 15% ether in pentane gave 262 mg (10%) of 2,3-diphenylindene, mp 110–112° (needles, lit.¹² 108–109°). The nmr¹² and uv²⁰ spectra were consistent with those previously reported: τ 6.15 (5.2); ir 1660 cm⁻¹ (C=C, weak); uv (95% EtOH) 233 nm (ϵ 34,200), 304 (31,000); mass spectrum *m/e* (rel intensity) 165 (10), 189 (13), 191 (15), 265 (15), 267 (25), 268 (100, M⁺), 269 (25).

Anal. Calcd for C₂₁H₁₆: C, 93.99; H, 6.01. Found: C, 93.02; H, 6.04.

Addition of ICl (0.498 g, 3.06 mmol) to 3,3-diphenylpropene (0.537 g, 1.98 mmol) in 12 ml of acetonitrile gave a product the nmr spectrum of which was nearly identical with that of pure 2,3-diphenylindene. Integration of the singlet at τ 6.15 (2 H) vs. the aromatic multiplet (14 H) indicates a yield of 92% for 2,3-diphenylindene (13).

exo-5-Azido-*anti*-7-iodobenzonorborene (19).—In a modification of general procedure 1.1 equiv. of IN_3 was allowed to react with 0.861 g of benzonorborene for 94 hr to furnish 1.85 g (99%) of the adduct, mp 58–67°. Prisms were obtained from ethanol: mp 77.5–78°; ir 2125 cm^{-1} (C–N₃); nmr τ 2.9 (s, 4), 5.96 (qui, 1), 6.37 (m, 3), 7.55 (2t, 1), 8.11 (d, 1); mass spectrum *m/e* (rel intensity) 63 (11), 115 (45, indenyl cation) 116 (10), 127 (23), 128 (49), 129 (100, dihydronaphthalene cation), 130 (15), 141 (4), 156 (19).

Anal. Calcd for $\text{C}_{11}\text{H}_{10}\text{IN}_3$: C, 42.46; H, 3.24. Found: C, 42.33; H, 3.30.

1-Iodomethyl-3-azidonortricyclane (21).—Adduct 21 (5.4 g 100%) was obtained from 2.12 g of methylene norbornene. The oil showed no vinylic protons in the nmr, turned dark at room

temperature and could not be purified by distillation: ir 2105 cm^{-1} (N₃); nmr τ 6.1 (s, 1), 6.53 (s, 2), 7.8–9.1 (m, 7); mass spectrum *m/e* (rel intensity) 39 (49), 41 (30), 51 (25), 53 (21), 54 (48), 65 (45), 66 (43), 67 (21), 77 (94), 78 (25), 79 (39), 91 (98), 93 (100), 120 (37), 141 (10, $\text{CH}_2=\text{I}^+$), 148 (24, $\text{M}^+ - \text{I}$).

Anal. Calcd for $\text{C}_8\text{H}_8\text{IN}_3$: C, 34.93; H, 3.66; I, 46.13; N, 15.28. Found: C, 33.92; H, 3.76; I, 44.80; N, 17.64.

Registry No.—1, 3282-07-3; 2, 25683-82-3; 3, 25683-83-4; 3 2,4-DNP, 25683-84-5; 5, 25683-85-6; 7, 25683-86-7; 8, 25683-87-8; 13, 5324-00-5; 19, 25683-89-0; 21, 25683-90-3.

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Coupling and Disproportionation Reactions of Cumyl Radical-Cyclohexyl Radical Pairs from α -Cumylazocyclohexane¹

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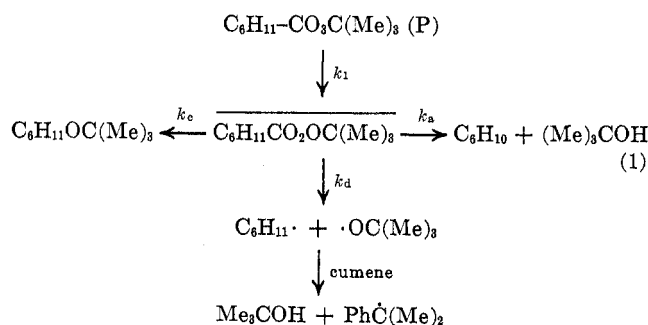
The new unsymmetrical azo compound, α -cumylazocyclohexane (A), has been synthesized and the products resulting from its thermal decomposition in cumene (110°) have been quantitatively determined. Products formed and their observed yields given in mol % based on the starting azo compound were cyclohexene (5%), cyclohexane (78%), α -cumylcyclohexane (21%), bicumyl (51%), and α -methylstyrene (4%). All of the cyclohexene, α -cumylcyclohexane, and ca. one-third of the cyclohexane are cage products giving a cage effect of ca. 0.50. The remaining cyclohexane arises *via* hydrogen abstraction from cumene by diffused cyclohexyl radicals. A comparison of these data with those for decomposition of carbo-*t*-butylperoxycyclohexane (*t*-butyl perester of cyclohexane carboxylic acid) in cumene permitted a detailed analysis of the origins of the products in both systems. The data from A give the relative rates of the coupling and the two available disproportionation reactions for a cyclohexyl radical-cumyl radical pair. These data for a mixed alkyl radical-aralkyl radical pair are compared with similar data for symmetrical alkyl radical pairs and aralkyl radical pairs and indicate that the high combination-disproportionation ratios observed for the latter are the result of a special property of a pair of aralkyl radicals.

As part of a continuing study of the effects of pressure on free radical reactions we have determined the pressure dependence of the cage effect associated with decomposition of various radical initiators.² One such initiator was the *t*-butyl perester of cyclohexane-carboxylic acid (carbo-*t*-butylperoxycyclohexane) (P) which decomposes by the two-bond scission mechanism shown in Scheme I.^{2b,d} In this system, the cage effect

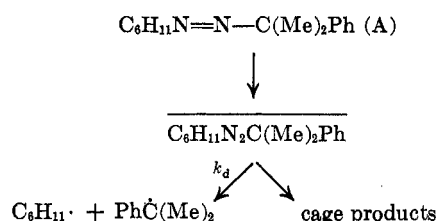
was calculated using the relative amounts of *t*-butyl cyclohexyl ether, cyclohexene, and *t*-butyl alcohol. While the results obtained were reasonable by comparison with other systems, we were unable to provide concrete evidence that cyclohexene arose only from the cage reaction shown in Scheme I. It also seemed possible that it could have been formed by disproportionation of a pair of cyclohexyl radicals, and/or a cyclohexyl and cumyl radical pair, subsequent to separative diffusion of the primary geminate cyclohexyl and *t*-butoxy radicals.

In order to provide data relating to the possible origin of cyclohexene from these latter reactions, we have synthesized the new compound α -cumylazocyclohexane (A) and have quantitatively determined the products arising from its thermal decomposition in cumene. The anticipated decomposition mechanism is outlined in Scheme II and it can be seen that this system should

SCHEME I



SCHEME II



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(2) (a) R. C. Neuman, Jr., and R. J. Bussey, *J. Amer. Chem. Soc.*, **92**, 2440 (1970); (b) R. C. Neuman, Jr., and J. V. Behar, *ibid.*, **91**, 6024 (1969); (c) R. C. Neuman, Jr., and R. J. Bussey, *Tetrahedron Lett.*, 5859 (1968); (d) R. C. Neuman, Jr., and J. V. Behar, *ibid.*, 3281 (1968); (e) R. C. Neuman, Jr., and J. V. Behar, *J. Amer. Chem. Soc.*, **89**, 4549 (1967).