the sake of completeness and comparison with the studies using N-bromosuccinimide.

**Calculations.**—The Hammett $\rho$-values were calculated from least squares slopes of the lines resulting from plots of log $k_X/k_0$ *vs.* $\sigma^+$ or *vs.* $\sigma^\circ$. The expected errors in $\rho$ and the correlation coefficients were calculated by standard statistical methods.[12]

**Relative Reactivity of Allylbenzene and Toluene toward N-Bromosuccinimide.**—The procedure and calculations were the same as those employed to study relative reactivities of the various allylbenzenes.

## Results and Discussion

In Table I are presented the relative rates of hydrogen abstraction from allylbenzenes by bromine atoms and trichlormethyl radicals. From the data in this Table it is possible to calculate reaction constants, that is $\rho$-values, for these reactions. The $\rho$-values, obtained by calculating the slopes of the regression lines resulting from plots of log $k_X/k_0$ *vs.* $\sigma^+$ or $\sigma^0$ are presented in Tables II and III. In the reaction with N-bromosuccinimide, the allylbenzenes were studied at a lower temperature than the toluenes (69.5° compared with 80°), whereas in the reaction with bromotrichloromethane, the allylbenzenes were studied at a higher temperature than the toluenes (69.5° compared with 50°). Since the magnitude of a $\rho$-value varies inversely with temperature below the isokinetic temperature, the $\rho$-values for the two systems in their reactions with N-bromosuccinimide would be further apart if studied at the same temperature than they are at the temperatures indicated in Table II, whereas for the reaction with bromotrichloromethane, the $\rho$-values would be nearer to each other in magnitude when studies at the same temperature, then they are at the temperatures indicated in Table III. Making allowances for the differences in temperatures at which these studies have been conducted, it would appear that hydrogen abstraction reactions from allylbenzenes have Hammett $\rho$-values of the order of one half to one-third as great in magnitude as those for abstraction from toluenes by the same radical.

TABLE I

RELATIVE RATES OF ABSTRACTION OF A HYDROGEN ATOM FROM SUBSTITUTED ALLYLBENZENES BY A BROMINE ATOM AND A TRICHLOROMETHYL RADICAL AT 69.5°

| Substituent | $\sigma^{0a}$ | $\sigma^{+b}$ | $k_X/k_0$ (Br·) | $k_X/k_0$ ($Cl_3C$·)[c] |
|---|---|---|---|---|
| *p*-$(CH_3)_2N$ | −0.44 | −1.700 | 20.9 ± 0.07[d] | |
| *p*-$CH_3O$ | −0.16 | −0.778 | 3.23 ± 0.20 | 1.46 ± 0.07[d] |
| *p*-$CH_3$ | −0.15 | −0.311 | 1.89 ± 0.04 | 1.42 ± 0.03 |
| *p*-$C_6H_5$ | 0.00 | −0.179 | 1.70 ± 0.03 | 1.02 ± 0.08 |
| *p*-F | +0.17 | −0.073 | 1.08 ± 0.02 | 0.94 ± 0.03 |
| *m*-$CH_3$ | −0.07 | −0.060 | 1.29 ± 0.13 | 1.15 ± 0.04 |
| H | 0.00 | 0.000 | 1.000 | 1.000 |
| *m*-$CH_3O$ | +0.13 | +0.047 | 1.02 ± 0.01 | 0.82 ± 0.01 |
| *p*-Cl | +0.27 | +0.114 | 0.78 ± 0.05 | 0.78 ± 0.05 |
| *m*-Cl | +0.37 | +0.339 | 0.50 ± 0.06 | 0.60 ± 0.01 |
| *m*-$CF_3$ | +0.42[e] | +0.562 | 0.40 ± 0.01 | 0.54 ± 0.02 |
| *p*-$CF_3$ | +0.55[e] | +0.612 | 0.36 ± 0.01 | 0.47 ± 0.01 |

[a] R. W. Taft, *J. Phys. Chem.*, **64**, 1805 (1960). [b] H. C. Brown and Y. Okamoto, *J. Am. Chem. Soc.*, **80**, 4979 (1958). [c] See ref. 10. [d] Average deviation. [e] $\sigma^0$ values are not available for *m*- and *p*-$CF_3$, but for strongly electron-withdrawing groups, $\sigma \approx \sigma^0$. The values indicated are $\sigma$ values; J. Hine, "Physical Organic Chemistry," McGraw-Hill Book Co., Inc., New York, N. Y., 1956, p. 72.

(12) W. J. Gore, "Statistical Methods for Chemical Experimentation," Interscience Publishers, Inc., New York, N. Y., 1952, Chap. 6.

TABLE II

$\rho$-VALUES FOR THE REACTIONS, Br· + $C_6H_5CH_2R$ ⟶ HBr + $C_6H_5\dot{C}HR$

| R | Temp., °C. | $\rho^{a}(r^{b})$ |
|---|---|---|
| $CH{=}CH_2$ | 69.5 | −0.76 ± 0.03 (−0.99) |
| H[c] | 80.0 | −1.39 ± 0.03 (−0.99) |

[a] Calculated using $\sigma^+$. [b] Correlation coefficient. [c] ref. 4.

TABLE III

$\rho$-VALUES FOR THE REACTIONS, $Cl_3C$· + $C_6H_5CH_2R$ ⟶ $HCCl_3$ + $C_6H_5\dot{C}HR$

| R | Temp., °C. | $\rho^{a}(r^{b})$ | $\rho^{c}(r^{b})$ |
|---|---|---|---|
| $CH{=}CH_2$ | 69.5 | −0.39 ± 0.03 (−0.94) | −0.58 ± 0.03 (−0.99) |
| H[d] | 50.0 | −1.46 | −1.72 (−0.99) |

[a] Calculated using $\sigma^+$. [b] Correlation coefficient. [c] Calculated using $\sigma^0$. [d] See ref. 7.

It was also found that allylbenzenes is 17.5 ± 1.1 times as reactive toward hydrogen abstraction by the bromine atom as toluene at 69.5°, reflecting the stabilizing effect of the $\alpha$-vinyl group. Comparing this figure with data recently published by Russell, Deboer, and Desmond,[9] it would appear that a hydrogen atom is more easily abstracted by a bromine atom from allylbenzene than from diphenylmethane. This is probably a consequence of the greater difficulty with which coplanarity is approached by the two phenyl groups of the diphenylmethyl radical compared to the phenyl group and vinyl group of the $\alpha$-vinylbenzyl radical.

**Acknowledgment.**—It is a pleasure to thank the Donors of the Petroleum Research Fund for a grant (PRF-603A) which financed the greater part of this work.

## Derivatives of 2-Benzyl-1-indanone. Competing Alicyclic and Aromatic Monobromination

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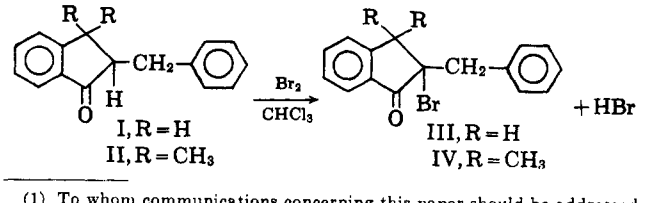
It has been shown previously that treatment of 2-benzyl-1-indanone (I) or 2-benzyl-3,3-dimethyl-1-indanone (II) with an equimolar quantity of bromine in chloroform leads to an excellent yield of the corresponding 2-bromo-2-benzyl-1-indanone.[2,3] The product controlling factor is the activating influence of the carbonyl group.




(1) To whom communications concerning this paper should be addressed.
(2) N. H. Cromwell and R. P. Ayer, *J. Am. Chem. Soc.*, **82**, 133 (1960).
(3) B. D. Pearson, R. P. Ayer, and N. H. Cromwell, *J. Org. Chem.*, **27**, 3038 (1962).

Condensation of *p*-dimethylaminobenzaldehyde with 1-indanone and quantitative hydrogenation of the 2-(*p*-dimethylaminobenzal)-1-indanone (V) at atmospheric pressure yielded 2-(*p*-dimethylaminobenzyl)-1-indanone (VI). In VI, in addition to the activated 2-position, the two aromatic hydrogens *ortho* to the *p*-dimethylamino group are also expected to be replaceable.

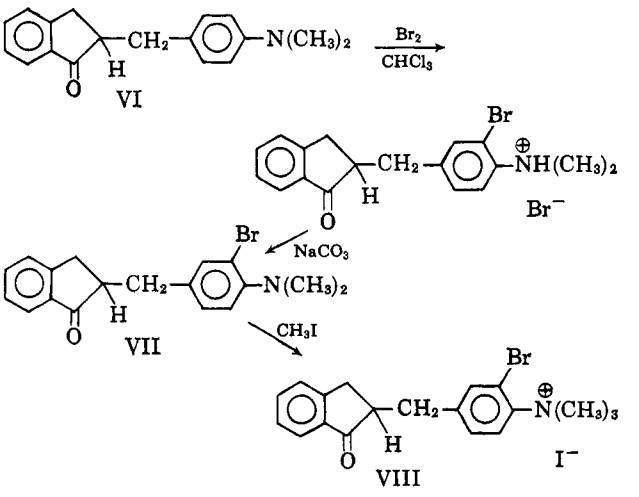
Bromination of IV produces a compound (VII) with analysis for a monobrominated derivative but which gives no reaction with piperidine in acetonitrile under conditions more rigorous than those in which 2-bromo-2-benzyl-1-indanone (III) gives a 100% yield of 2-benzal-1-indanone.[4] Similarly, conversion of VII to its methiodide (VIII) followed by attempted reaction of VIII with excess bromide ion in acetonitrile gave no reaction under conditions in which III gives 100% acid formation and at least a 90% yield of 2-benzal-1-indanone.

If the monobromoindanone VII was 2-bromo-2-(*p*-dimethylaminobenzyl)-1-indanone then the results would indicate that relative to the parent compound III, both electron-supplying ($-NMe_2$) and electron-withdrawing ($-N^+Me_3$) groups introduced into the *para* position of the benzyl group cause an enormous reduction in the rate of exocyclic dehydrobromination reactions. It is clear that the bromine has been introduced other than into the 2-position and into a position where it is immune from attack by nucleophilic reagents. The results point to aromatic bromination, and this is confirmed by consideration of proton magnetic resonance spectra.

In deuteriochloroform, 2-benzyl-1-indanone (I) and 2-(*p*-dimethylaminobenzyl)-1-indanone (VI), both give a complex splitting pattern in the region 6.5–7.8 $\tau$ due to five protons, the two methylene protons in the 3-position, the tertiary proton in the 2-position, and the two *exo* benzylic methylene protons. Bromination of I in the 2-position, to give III, leads to isolation of the two methylene groups and a much simpler splitting pattern, arising only from nonequivalence of protons within the methylene groupings.

Bromination of VI leads to VII in which the splitting pattern in the region 6.5–7.8 $\tau$ is unaltered. Major changes are, however, produced in the pattern of the aromatic protons, which now integrate for only seven protons showing that aromatic bromination has taken place. Two doublets at 3.35 and 2.90 $\tau$ ($J$ = 8 c.p.s.) arising from two superimposed AB systems of aromatic protons in the *para* substituted benzyl group of VI are absent after bromination, and, in particular, no peaks due to aromatic protons are observed above 3.1 $\tau$. It is clear that the activating influence exerted upon the aromatic hydrogens *ortho* to the *p*-dimethylamino group is sufficient to divert the bromination away from the carbonyl activated 2-position. (See col. 2.)

**Proton Magnetic Resonance Spectra in Trifluoroacetic Acid.**—Dimethylamino derivatives are protonated in trifluoroacetic acid, and the spectra are different in character from those observed in deuteriochloroform. The signal due to the six methyl protons is split by the proton on the nitrogen, and the protons of the benzyl aromatic ring are subjected to a very different substituent shielding effect. No signal corresponding to the quaternary ammonium proton could be detected.




The dimethylanilinium ion gives a signal corresponding to six methyl protons at 6.52 $\tau$ ($J$ = 5 c.p.s.) and a fairly sharp signal corresponding to all five aromatic protons at 2.35 $\tau$. 2-(*p*-Dimethylaminobenzyl)-1-indanone (VI) has absorption due to six methyl protons at 6.51 $\tau$ ($J$ = 5 c.p.s.) and several peaks of moderate intensity in the range 2.0–2.7 $\tau$ with superimposed one sharp and intense peak, corresponding to four benzylic aromatic protons, at 2.38 $\tau$. The monobromination product VII has absorption due to six methyl protons at 6.46 $\tau$ ($J$ = 5 c.p.s.) and several aromatic peaks of moderate intensity in the range 2.0–2.6 $\tau$. The shift of the methyl proton signal and the disappearance of the sharp and intense signal in the aromatic region upon monobromination is consistent with formulation as 2-(*m*-bromo-*p*-dimethylaminobenzyl)-1-indanone (VII).

The methiodide of VII (VIII) gives several peaks of moderate intensity in the range 2.0–2.7 $\tau$ and a sharp peak corresponding to the nine methyl protons at 6.00 $\tau$.

For VI, VII, and VIII in addition to the peaks mentioned previously a complex splitting pattern arising from five nonaromatic protons was observed in the range 6.2–7.2 $\tau$.

**Proton Magnetic Resonance Spectra of Aromatic Protons in Methanol.**—In methanol 2-(*p*-dimethylaminobenzyl)-1-indanone (VI) gives several moderately intense peaks corresponding to four indanone aromatic protons in the region 2.2–2.8 $\tau$ and two doublets ($J_{AB}$ = 8 c.p.s.) corresponding to two protons *ortho* and two protons *meta* to the dimethylamino group at 3.37 and 2.95 $\tau$. In the presence of 0.2 $M$ hydrobromic acid the doublets disappear, and, consistent with the spectrum in trifluoroacetic acid, a new sharp and intense peak occurs at 2.58 $\tau$, superimposed upon a background of moderately intense peaks in the region 2.2–2.7 $\tau$.

2-(*m*-Bromo-*p*-dimethylaminobenzyl)-1-indanone (VII) gives a complex system of peaks in the region 2.1–3.1 $\tau$ which in the presence of 0.2 $M$ hydrobromic acid gives a differing pattern of moderately intense peaks in the region 2.0–2.7 $\tau$. The methiodide of VII (VIII) gives a doublet ($J$ = 8 c.p.s.) corresponding to one proton at 2.04 $\tau$ and peaks corresponding to six other protons in the region 2.2–2.8 $\tau$.

(4) G. A. Coppens, D. N. Kevill, and N. H. Cromwell, unpublished results.

### Experimental[5]

**2-(*p*-Dimethylaminobenzal)-1-indanone (V).**—To an ice-cooled solution of 7.94 g. (0.0600 mole) of 1-indanone dissolved in 20 ml. of ethanol was added slowly an ice-cooled solution of 0.34 g. of potassium hydroxide (0.0060 mole) and 8.95 g. (0.0600 mole) of *p*-dimethylaminobenzaldehyde in 50 ml. of ethanol. The mixture was allowed to stand overnight in a refrigerator. Filtration and washing with ethanol gave 15.0 g. (99% yield) of yellow crystals, m.p. 161–162°. After recrystallization from dioxane, it had m.p. 164–165°; $\lambda_{max}$ 271, 431 mμ (ε 17,400, 36,600); $\nu_{C=O}$ 1698 vs (1690 vs in acetonitrile), $\nu_{C=C}$ 1629 m, $\nu_{Ar}$ 1605 cm.$^{-1}$ vs.

The proton magnetic resonance spectrum in deuteriochloroform shows six methyl protons at 7.05 τ, two methylene protons (split by 2 c.p.s.) at 6.13 τ, two equivalent aromatic protons (*ortho* to the dimethylamino group and split by two equivalent protons *meta* to this grouping; $J$ = 8 c.p.s.) at 3.37 τ, peaks corresponding to five aromatic and one vinyl proton in the range 2.3–2.9 τ, and the aromatic proton beta to the carbon group (split by the γ proton; $J$ = 7 c.p.s.) at 2.15 τ.

*Anal.* Calcd. for $C_{18}H_{17}ON$: C, 82.10; H, 6.51; N, 5.32. Found: C, 82.32; H, 6.50; N, 5.26.

**2-(*p*-Nitrobenzal)-1-indanone.**—The same procedure as for V was followed, but using 9.07 g. (0.0600 mole) of *p*-nitrobenzaldehyde. Obtained was 12.8 g. (80% yield) of pale yellow crystals, m.p. 228–230°. Recrystallization from glacial acetic acid gave long pale yellow needles which were washed with petroleum ether and ether, m.p. 251–252°; $\lambda_{max}$ 321 mμ; $\nu_{C=O}$ 1692 cm.$^{-1}$ (KBr pellet and LiF optics).

*Anal.* Calcd. for $C_{16}H_{11}O_3N$: C, 72.44; H, 4.18; N, 5.28. Found: C, 72.22; H, 4.14; N, 5.41.

**2-(*p*-Dimethylaminobenzyl)-1-indanone (VI).**—To a solution of 9.0 g. of 2-(*p*-dimethylaminobenzal) 1 indanone (V) in 900 ml. of dioxane was added 0.9 g. of 10% palladium on charcoal. The mixture was heated to 45–50° and quantitative hydrogenation carried out at atmospheric pressure. The solution was filtered and evaporated to dryness to give gray-brown crystals. Recrystallization from ethanol gave 6.4 g. (70% yield) of almost colorless crystals, m.p. 77–79°. Several additional recrystallizations raised the m.p. to 79–80°; $\lambda_{max}$ 249, 293 mμ (ε 32,000, 6,700); $\nu_{C=O}$ 1715 vs (1710 cm.$^{-1}$ vs in acetonitrile), $\nu_{Ar}$ 1619 cm.$^{-1}$ s.

The p.m.r. spectrum in deuteriochloroform shows a sharp peak corresponding to six methyl protons at 7.12 τ, several peaks corresponding to five protons in the range 6.5–7.8 τ, two protons *ortho* and two protons *meta* to the dimethylamino group (constituting two superimposed AB systems; $J_{AB}$ = 8 c.p.s.) at 3.35 and 2.90 τ, respectively, peaks corresponding to three aromatic protons in the range 2.4–2.9 τ, and the aromatic proton beta to the carbonyl group at 2.27 τ ($J$ = 7 c.p.s.).

*Anal.* Calcd. for $C_{18}H_{19}ON$: C, 81.47; H, 7.22; N, 5.28. Found: C, 81.53; H, 7.28; N, 5.34.

**2-(*m*-Bromo-*p*-dimethylaminobenzyl)-1-indanone (VII).**—To a solution of 21.2 g. (0.0800 mole) of 2-(*p*-dimethylaminobenzyl)-1-indanone (VI) in 75 ml. of chloroform was added over a period of 1 hr. with stirring and in the presence of sunlight, a solution of 12.8 g. (0.0800 mole) of bromine in 25 ml. of chloroform. After standing for an additional 30 min. the solution was evaporated and the product recrystallized from ethanol to give 25.8 g. (76% yield) of the hydrobromide of VII. This product, m.p. 123°, was hygroscopic and gave an instantaneous precipitate with alcoholic silver nitrate; $\lambda_{max}$ 246, 287 mμ (ε 19,800, 4800); $\nu_{C=O}$ 1712 cm.$^{-1}$ vs (in acetonitrile).

Extraction of 10 g. of the hydrobromide by 150 ml. of 5% aqueous sodium carbonate and 100 ml. of ether, washing the ether layer, drying over anhydrous magnesium sulfate, and evaporation gave 7.5 g. (81% yield) of crude VII. Recrystallization from ether–petroleum ether gave pure VII, m.p. 71–72°; $\lambda_{max}$ 247, 289 mμ (ε 30,500, 8100); $\nu_{C=O}$ 1719 vs, $\nu_{Ar}$ 1614 cm.$^{-1}$ m.

The p.m.r. spectrum in deuteriochloroform shows a sharp peak corresponding to six methyl protons at 7.22 τ, several peaks corresponding to five protons in the range 6.5–7.8 τ, a complex series of peaks corresponding to six aromatic protons in the range 2.4–3.1 τ, and the signal from the aromatic proton beta to the carbonyl at 2.23 τ ($J$ = 7 c.p.s.).

*Anal.* Calcd. for $C_{18}H_{18}ONBr$: C, 62.80; H, 5.27; N, 4.07. Br, 23.22. Found: C, 62.99; H, 5.35; N, 4.17; Br, 23.01.

An acetonitrile solution 0.01 *M* in VII and 0.03 *M* in piperidine, maintained in sealed bulbs at 91.9°, underwent no reaction as measured either by reduction in base concentration or by increase in bromide ion concentration[6] during a period of 30 hr.

**2-(*m*-Bromo-*p*-dimethylaminobenzyl)-1-indanone Methiodide (VIII).**—A mixture of 20 ml. of ethanol, 15 ml. of methyl iodide, and 7.0 g. of 2-(*m*-bromo-*p*-dimethylaminobenzyl)-1-indanone (VII) was maintained in a sealed tube at 60° for 15 hr. and then allowed to stand at room temperature for 2 days. Ether extraction left 2.8 g. (28% yield) of crude VIII. Recrystallization from ethanol gave pure VIII, m.p. 152–153°; $\lambda_{max}$ 242, 295 mμ (ε 25,700, 4700).

*Anal.* Calcd. for $C_{19}H_{21}ONBrI$: C, 46.92; H, 4.35; N, 2.88; Br + I, 42.54. Found: C, 47.01; H, 4.45; N, 2.92; Br + I, 42.70.

Neither an acetonitrile solution 0.0082 *M* in VIII nor an acetonitrile solution 0.0041 *M* in VIII and 0.0239 *M* in tetraethylammonium bromide developed any acidity[6] during 3 days in sealed bulbs at 91.9°.

**Acknowledgment.**—This work was supported in part by Grant No. G-14469, National Science Foundation.

(5) Melting points were read with a calibrated thermometer. Infrared spectra were measured with a Perkin-Elmer Model 21 double beam recording instrument employing, unless otherwise stated, sodium chloride optics and matched sodium chloride cells with carbon tetrachloride solutions. The ultraviolet spectra were determined with a Cary Model 11-MS recording spectrophotometer using reagent grade methanol solutions. The proton magnetic resonance spectra were obtained with a Varian A-60 instrument *using a trace of tetramethylsilane (τ 10.00) as internal reference.*

(6) Acid–base titrations in acetone using Lacmoid, *i.e.*, resorcinol blue, as indicator. Bromide titrations by potentiometric titration in acidified acetone against aqueous silver nitrate.

## A Convenient Method for Utilizing the Allyl Grignard Reagent

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*Received April 11, 1963*

It is the purpose of this paper to point out and emphasize a convenient synthetic technique which has been known for a number of years but has been overlooked and even discouraged. The method of utilizing the allyl Grignard reagent reported here has been referred to as the Barbier–Grignard procedure.[1] In this procedure the organomagnesium compound is not formed as an intermediate in the presence of an excess of carbonyl compound as Barbier[2a,3,4] did, nor is the functional addend withheld until the preparation of the Grignard reagent is complete. Rather a solution of the alkyl halide and the functional addend is added to the magnesium metal to which a small amount of allyl halide has been added to start the reaction; there is no large excess of carbonyl compound present at any time. The application of the Barbier–Grignard procedure to allylic halides has been employed periodic-

(1) H. R. Henze, B. B. Allen, and W. B. Leslie, *J. Org. Chem.*, **7**, 326 (1942).

(2) M. S. Kharasch and O. Reinmuth, "Grignard Reactions of Nonmetallic Substances," Prentice-Hall, Inc., New York, N. Y., 1954, (a) p. 3; (b) p. 27; (c) p. 143.

(3) G. H. Richter, "Textbook of Organic Chemistry," John Wiley and Sons, Inc., New York, N. Y., 1938, p. 170.

(4) P. Barbier, *Compt. rend.*, **128**, 110 (1899).